SS Protocol

SOIL SOLUTION CHEMISTRY (SS)

Aim

To monitor changes in the chemical composition of soil solution using suction lysimeters

Rationale

Soil solution chemistry is likely to be affected by physical and chemical changes in the environment and itself to have important effects on ecosytem processes; for example, soil temperature and moisture status strongly influence the microbial activity in soil which controls nutrient release into the soil solution (Swift, Heal & Anderson 1979). In turn, soil solution nutrient status has a major influence on plant productivity and thus on animal productivity.

The commonly used non-destructive methods of soil solution sampling can be divided into zero tension methods and suction methods. Zero tension methods use a volume of soil contained in such a way that water percolating through the soil drains into a collecting vessel. These methods are suitable for leaching studies, where the objective is to quantify nutrients being lost from the soil (Addiscott 1990). Suction methods involve the insertion into the soil of a porous-walled sampler which is evacuated so that water is drawn into it. Suction samplers collect water whether or not it is percolating through the soil and were termed 'artificial roots' by early researchers (Briggs & McCall 1904). For the purposes of ECN, it has been thought most appropriate to sample water which equates approximately with that which is available to plants, and accordingly suction sampling is being used.

Ceramic suction samplers have been criticised because the chemical composition of the soil solution can be modified by contact with the ceramic material (Raulund-Rasmussen 1989), and for this reason samplers manufactured by Prenart from PTFE and quartz are specified. The small size of Prenart samplers makes them suitable for installation in the wide variety of soils encountered at ECN sites; larger and more intrusive types of sampler would result in hydrological disruption and aeration of peat soils, and would be impossible to install at the base of shallow soils, in stony soils and in soils containing tree roots.

Suction samplers are not without operational problems, a number of which were identified by Hanson and Harris (1975), who also suggested procedures to overcome them. While factors such as soil texture can influence the characteristics of the soil solution collected at a site, this is likely to be of minor importance in an environmental change study because the main emphasis here is on temporal variation rather than on between-site variation. 'Plugging' of the sampler pores by soil particles may cause the performance of samplers at some sites to change through time; in order to monitor this possibility the volume of water collected and the residual vacuum must be recorded. A procedure for sampler replacement is included in this Protocol.

Method

Equipment

Prenart 'super quartz' soil water samplers are manufactured from PTFE and silica flour. They are cylindrical, 21 mm in diameter and 95 mm in length, conical at one end and with a tube attachment at the other. The tubing links the sampler to a 1 litre glass collecting bottle with a Prenart screw cap. The collecting bottles are placed in an insulated box to protect the samples from extremes of temperature and are evacuated using a portable pump. Details of the equipment required are provided in Appendix I.

Location

Samplers will be located within a 6 m x 6 m plot which is itself located within a 10 m x 10 m plot on the edge of, but outside, the TSS. On sloping sites the plot will ideally be located on the downslope edge of the TSS and definitely not on the upslope edge, so as to avoid any debris from soil disturbance and trampling being washed on to the TSS. Although no permanent location markers are used within the 10 m x 10 m plot, it should be envisaged as being divided into 1 m x 1 m cells, as shown in Figure 10.

Six samplers will be installed in the A horizon and six others at the base of the B horizon. The conical base of the sampler can be allowed to penetrate the horizon below the one being sampled, but the porous section of the sampler should not do so. Where these horizons do not exist (eg in peat soils) depths of 10 cm and 50 cm will be used. In shallow soils where these horizons do not exist, the upper samplers will be installed at 10 cm and the lower samplers at the base of the soil. In soils less than 20 cm in depth, only one set of six samplers will be installed, at a depth of 10 cm. These soil depths are depths below and perpendicular to the surface, and refer to the position of the mid-point along the length of the sampler.

The procedure for selecting cells to receive samplers and also for the rolling programme of sampler replacement is described in Appendix II. Each selected cell will have both a deep and a shallow sampler located according to Figure 11. Samplers should be identified by a three-character code, where the first character is the letter co-ordinate for the cell (as given in Figure 10), the second character is the number co-ordinate for the cell and the third character is either 'S' for shallow or 'D' for deep. The installation procedure is described in Appendix III. Trampling within the plot during sampling should be minimised, though animals grazing the TSS should also have access to the soil solution sampling plot.

Sampling

The detailed procedure for collecting samples is provided in Appendix IV. Samplers will be emptied and water volumes recorded on the same day each fortnight, synchronised to coincide with Wednesday, 3 January 1996. One week after sample collection the samplers should be evacuated to 0.5 bar; thus the water sample accumulates over only the second week of the fortnightly period. In some clay soils this partial vacuum will be insufficient to extract a sufficient quantity of soil solution to allow chemical analysis; if this is found to be the case after several weeks of wet weather, then a vacuum of 0.7 bar should be applied following agreement with the ECN Central Co-ordination Unit; subsequent sampling at such sites should always be at 0.7 bar.

Ideally soil solution should be collected throughout the year but in dry periods the volume of extracted water will decrease and eventually no further water will be extractable. Some sites will be particularly prone to this condition and, even in an average summer, there may be a substantial period when no water is extracted. There is little point in continuing fortnightly evacuation during such periods but it is important to ensure that sampling is resumed as soon as the soil becomes sufficiently wet because early samples are likely to have particularly high nutrient concentrations. Close attention should therefore be paid to meteorological data from the site and the vacuum appropriate to the site should be applied periodically to determine whether water can be extracted. The dates of these vacuum checks, and their results, should be included with the normally formatted soil solution data forwarded to the ECN database. The standard fortnightly evacuation routine should be operated regularly at all sites from the beginning of October to the end of May, irrespective of soil moisture status.

At some sites, particularly in late spring and in autumn, the volume of water collected may be very small and it may be necessary to discard very small samples, or combine the six samples for analysis. The following rule will be used.

- If the volume collected from any individual sampler is less than 10 ml, it should be discarded.

- If, for a particular soil depth, the volume collected by three or more samplers exceeds 60 ml, samples will be treated individually.

- Otherwise, all samples from that depth will be combined in the laboratory to make a single, combined sample.

Where samples are to be combined, the single combined sample from the shallow soil water samplers will be coded 'XXS' and from the deep soil water samplers 'XXD'.

Conductivity and pH are measured on unfiltered water according to methods in the Initial Water Handling (WH) Protocol, which also deals with filtering of the sample. After filtering, the water is analysed for dissolved Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Al^{3+}, NH_4^{+}-N, Cl^{-}, NO_3^{-}-N, SO_4^{2-}-S, PO_4^{3-}-P, alkalinity and dissolved organic carbon.

Labelling

Each water sample is identified uniquely by:
- the ECN Measurement Code (SS),
- the ECN Site ID Number (eg 04 for Moor House),
- the Location Code (eg 01), and
- the collection date ('Sampling Date') (eg 01-Jan-1996).

This information MUST be marked on the sample bottle, so that it can be used to identify the sample through its various analytical stages, and it must accompany the results when transferred to the ECN database.

Washing equipment

Bottle washing is described in the WH Protocol. The glass collecting bottles attached to the samplers must be washed in the laboratory at six-monthly intervals.

Safety note

Although the suction samplers do not use a high vacuum and the bottles are of toughened glass, there still exists a small risk of injury from bottle implosion. Appropriate safety precautions should therefore be taken, including the checking of bottles for cracks in the glass if, for example, the bottles have been dropped or if it is possible that the contents have been frozen.

Author

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References

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Raulund-Rasmussen, K. 1989. Aluminium contamination and other changes of acid soil solution by means of porcelain suction cups. *Journal of Soil Science*, **40**, 95-101.

Swift, M.J., Heal, O.W. & Anderson, J.M. 1979. *Decomposition in terrestrial ecosystems*. (Studies in Ecology, vol. 5.) Oxford: Blackwell Scientific.

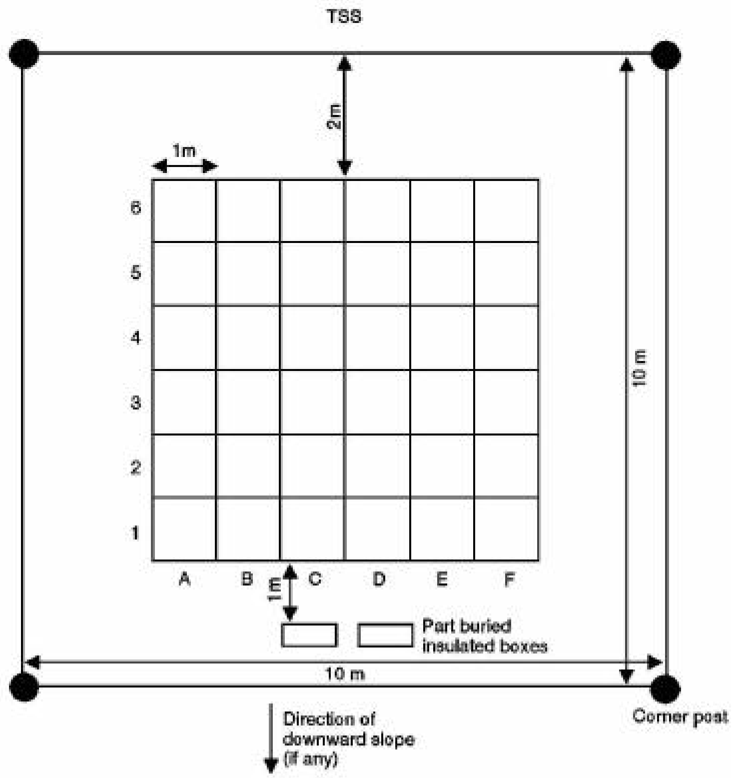

Figure 10. Layout of soil solution sampling area

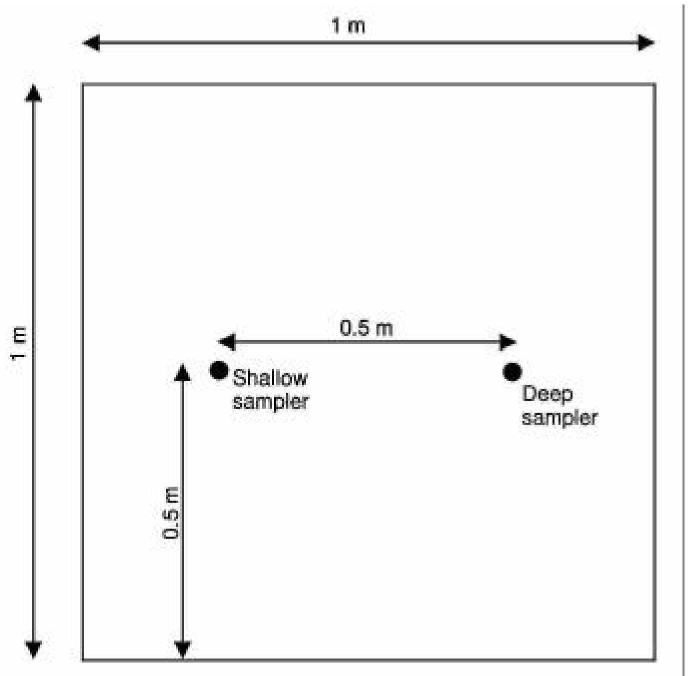

Figure 11. Location of samplers within a 1 m x 1 m cell

Appendix I. Equipment details (including spares)

Materials

- Prenart 'super quartz' soil water samplers, each with 10 m tubing attached (14)
- Pyrex 1 litre collecting bottles with Prenart screw caps (14)
- Battery-driven 12 volt vacuum pump with charger

Supplier

Prenart Equipment ApS
Buen 14
K-2000 Frederiksberg *Tel: 01045 3174 1664*
DENMARK *Fax: 01045 4280 3607*

It should be specified clearly that 10 m of tubing is required on each sampler.

Appendix II. Sampler location and replacement

The sampling arrangement uses some of the properties of the Latin square design. It has the advantages of simplicity, together with the desirable property of an element of randomness for future analysis.

The 6 m x 6 m area into which the soil solution samplers are placed is subdivided into 1 m x 1 m cells. In Year 1 the samplers are placed at two depths in the U cells.

After the first five years samplers in three of the cells, chosen at random, are abandoned and replaced by other samplers in three of the V cells in either the rows or columns. Following replacement either each row or each column will contain a cell with samplers.

After the next five years the remaining samplers in U cells are abandoned and replaced by samplers in the remaining V cells. Each row and column now contains a cell with a sampler.

This procedure is continued in succeeding five-year periods until all 36 cells have been exhausted. The cells in use are underlined in the following diagrams.

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Year 1

6	W	Y	Z	<u>U</u>	V	X
5	X	V	<u>U</u>	W	Y	Z
4	V	Z	W	X	<u>U</u>	Y
3	<u>U</u>	W	Y	Z	X	V
2	Z	X	V	Y	W	<u>U</u>
1	Y	<u>U</u>	X	V	Z	W
	A	**B**	**C**	**D**	**E**	**F**

SS Protocol

Year 6

6	W	Y	Z	U	$\underline{V}$	X
5	X	V	$\underline{U}$	W	Y	Z
4	V	Z	W	X	$\underline{U}$	Y
3	U	W	Y	Z	X	$\underline{V}$
2	Z	X	V	Y	W	$\underline{U}$
1	Y	U	X	$\underline{V}$	Z	W
	A	**B**	**C**	**D**	**E**	**F**

Year 11

6	W	Y	Z	U	$\underline{V}$	X
5	X	$\underline{V}$	U	W	Y	Z
4	$\underline{V}$	Z	W	X	U	Y
3	U	W	Y	Z	X	$\underline{V}$
2	Z	X	$\underline{V}$	Y	W	U
1	Y	U	X	$\underline{V}$	Z	W
	A	**B**	**C**	**D**	**E**	**F**

Year 16

6	$\underline{W}$	Y	Z	U	V	X
5	X	$\underline{V}$	U	W	Y	Z
4	$\underline{V}$	Z	W	X	U	Y
3	U	$\underline{W}$	Y	Z	X	V
2	Z	X	$\underline{V}$	Y	W	U
1	Y	U	X	V	Z	$\underline{W}$
	A	**B**	**C**	**D**	**E**	**F**

Appendix III. Installation of equipment

Materials

- Water samplers, each with 10 m of tubing attached (12)
- Collecting bottles with caps (12)
- Joiner's auger, 0.75 inch or 2 cm diameter with extended handle for deeper samplers
- Plastic pipe, maximum diameter 2 cm
- Distilled or deionised water
- Plastic beaker (3 of approximately 1 litre)
- Thin orange polypropylene string
- Insulated picnic boxes (2) each to contain six collecting bottles with holes drilled according to para 11 below
- Spade
- Soil sieve (2 mm)
- Vacuum pump
- Canes (24) for temporary marking of plot
- Measuring tape

Procedure

1. New Prenart soil water samplers are already rinsed in HCl and deionised water, ready for installation.

2. Sink the insulated boxes into the soil as indicated in Figure 10 so that only the lids and 5 cm of the walls protrude above the ground surface. While doing this the profile can be examined and soil obtained for para 3 below.

3. Sieve soil from all the horizons encountered. The soil should not be dried prior to sieving and it will usually be necessary to force the soil through the sieve, for instance with a rubber bung.

4. Mix, in the plastic beaker, a thin slurry of water and sieved soil from the horizon into which the sampler is to be placed.

5. Place the soil water sampler in the slurry and apply 0.5 bar vacuum for 10-15 minutes. This ensures that the biggest pores in the sampler are filled with fine soil and that there is a tight capillary contact with the soil.

6. Make a hole with the auger at an angle of 60° to the soil surface until the appropriate horizon/depth is reached. This angle ensures that the soil over the sampler is undisturbed.

7. Mix a thicker slurry of water and sieved soil from the horizon into which the sampler is to be placed and pour it into the hole using the funnel. The tubing attached to the funnel should extend to the bottom of the hole.

8. Tie the string to the top fitting of the sampler leaving enough string so that a loop extends approximately 5 cm above the ground surface. This serves to mark the location of the sampler and aid its removal should this be necessary.

9. Put the tube from the sampler and the marker string through the plastic pipe and push the sampler down the hole with the pipe, using the string to hold the sampler tightly against the bottom of the pipe.

10. Back-fill the hole with thick slurry made with sieved soil from the appropriate horizons.

11. Tubing from each sampler should be routed directly to the downhill boundary of the 1 m x 1 m cell in which it is located, and it should then follow cell boundaries to an insulated box. In most cases the full 10 m of tubing will not be required to link sampler and bottle. However, the excess tubing should not be cut off but rather coiled under a turf adjacent to the insulated boxes.

To minimise the impact of frost and animals, the tubing should be placed in the bottom of a 10 cm deep slit cut in the ground with the spade. The holes in the boxes should allow the tubing to enter without it having to emerge above the ground. These holes should be a tight fit around the tubing to prevent soil or water entering the boxes. In soils which frequently have high water tables there is a danger of the boxes floating. This can be obviated by enlarging the hole and placing at the bottom a plank of wood approximately 150 cm x 30 cm x 5 cm to which the boxes are tied. The plank and boxes are held in place by back-filling the soil.

12. Connect the tubing to the collecting bottles and evacuate the bottles to 0.5 bar using the pump.

13. The depth of the samplers and the layout of the tubing should be carefully recorded for future reference.

Some site conditions may require different installation procedures and experimentation with a limited number of samplers to find the most appropriate procedures is advisable. For peat soils the slurry will not be required; the fibrous peat surface should be penetrated with the auger and the sampler should then be pushed through undisturbed peat to the appropriate depth; if necessary, the hole above the sampler should be back-filled by poking solid peat down with the installation pipe. Where the samplers are installed close to the soil surface because the A horizon is shallow, it may be most appropriate to angle the samplers so they are almost horizontal. Where the string is likely to be damaged, for instance by grazing animals, it should still be installed to allow removal of the samplers but it should be protected by leaving the upper end below the ground surface with the tubing.

Appendix IV. Routine sample collection

Materials

- 250 ml polypropylene bottles, pre-marked with sampler codes (12)
- Vacuum pump (fully charged)
- Recording sheet and pencil

Procedure

1. Connect the pump to a collecting bottle and open the pinch clip. Ensure that the tubing walls have separated and record any residual vacuum.

2. Remove the collecting bottle and record the quantity of water it contains, using the calibrations on the bottle.

3. Fill the polypropylene bottle labelled with the corresponding sampler code and secure its cap.

4. Discard any water remaining in the collecting bottle away from the sampling square, ensuring that as much water as possible is removed from the bottle.

5. Re-connect the collecting bottle, in preparation for evacuation one week later.

6. One week after collecting the sample for analysis, attach the vacuum pump and establish the required vacuum (see under **Sampling**). The Database Manager should be informed of the vacuum being used. The vacuum should be read with the pump switched off because the gauge gives a false value when the pump is operating.

Specification of results and recording conventions

The measurement variables listed below are those required for each SS sampling location at an ECN Site. Sites submitting data to the ECNCCU should refer to the accompanying Data Transfer documentation for the specification of ECN dataset formats, available on the restricted access Site Managers' extranet. Contact ecnccu@ceh.ac.uk if you need access to this documentation.

The first 4 key parameters uniquely identify a sample or recording occasion in space and time, and must be included within all datasets:

• Site Identification Code (e.g. T05)	Unique code for each ECN Site
• Core Measurement Code (e.g. PC)	Unique code for each ECN 'core measurement'
• Location Code (e.g. 01)	Each ECN Site allocates its own code to replicate sampling locations for each core measurement (e.g. for different surface water collection points)
• Sampling Date (/time)	Date on which sample was collected or data recorded. This will include a time element where sampling is more frequent than daily

ECNCCU 2001

Core measurement: soil solution chemistry (SS Protocol)

The following variables are recorded from fortnightly samplings for each of 12 soil solution samplers.

Variable	Units	Precision of recording
Site Identification Code		
Core Measurement Code		
Location Code		
Setting out[1] date		
Setting out time	GMT 24-h clock	1 min
Sampling date		
Sampling time	GMT 24-h clock	1 min
Sampler code	3-character code (see SS Protocol, page 77)	
Volume	ml	10
Vacuum	bars	0.01
pH	pH scale	0.1
Conductivity	$\mu S\ cm^{-1}$	0.1
Alkalinity	$mg\ l^{-1}$	3 significant figures
Na^{+}	$mg\ l^{-1}$	3 significant figures
K^{+}	$mg\ l^{-1}$	3 significant figures
Ca^{2+}	$mg\ l^{-1}$	3 significant figures
Mg^{2+}	$mg\ l^{-1}$	3 significant figures
Fe^{2+}	$mg\ l^{-1}$	3 significant figures
Al^{3+}	$mg\ l^{-1}$	3 significant figures
PO_4^{3-}–P	$mg\ l^{-1}$	3 significant figures
NH_4^{+}–N	$mg\ l^{-1}$	3 significant figures
Cl^{-}	$mg\ l^{-1}$	3 significant figures
NO_3^{-}–N	$mg\ l^{-1}$	3 significant figures
SO_4^{2-}–S	$mg\ l^{-1}$	3 significant figures
Dissolved organic carbon	$mg\ l^{-1}$	3 significant figures

Recording forms
A standard field recording form is available from the CCU.
Note
1 Date/time vacuum 'drawn-down'.