

Aim *Collection of weekly stream/river water samples for analysis of major cations and anions*

Rationale The possible causes and consequences of changes in climate, land use and industrial, urban and agricultural pollution can be expected to be indicated by changes in the physical and chemical composition of water in rivers and streams. These are determined by both biogeochemical processes and by changes in terrestrial or atmospheric inputs. In addition to the major ions (eg Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} -S, alkalinity) which give a measure of the fundamental chemical composition of the water, other variables (eg NH_4^+ -N, NO_3^- -N, PO_4^{3-} -P) are major plant nutrients, whilst yet others (eg Al_3^+) have chemical states which are pH dependent and are of particular interest where water bodies are undergoing acidification. By measuring concentrations of these ions at frequent and regular intervals, together with water flow, it is possible to calculate loads and fluxes of ions which may be of interest in relation to nutrient budgets.

Method **Location**

Dip samples of flowing river water should be taken from at least one representative site above the weir, the location of which should be recorded and used for sampling on each occasion.

Sampling

Weekly samples will be collected on the same day each week, preferably on Wednesdays so as to synchronise with other ECN water collections (see PC and SS Protocols), within one hour of a time, to be specified for each site, which will depend on site accessibility. One 250 ml sample of river water will be taken from flowing water, using the same location on each occasion. The collecting bottle will be rinsed with river water, shaken vigorously with the stopper in place, and then the rinse-water will be discarded. The bottle is filled, leaving no air space, by reaching upstream. Stage height will be recorded at the time of sampling to the nearest 2mm. Conductivity and pH will be measured on unfiltered water according to methods described in the Initial Water Handling (WH) Protocol which also describes the filtering and subsequent treatment of the sample before further analysis.

After filtering, the water is analysed for 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.

Washing equipment

Procedures for bottle washing are described in the Initial Water Handling (WH) Protocol.

Labelling

Each water sample is identified uniquely by:

- the ECN Measurement Code (WC),
- the ECN Site ID Code (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.

Continuous monitoring

It is intended that continuous measurements of stream or river water temperature, conductivity, pH and turbidity should be carried out at suitable ECN sites. Instruments for this purpose are being tested and an ECN specification will be drawn up when satisfactory sensors have been identified.

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Specification of results and recording conventions

The measurement variables listed below are those required for each WC 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

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Core measurement: surface water chemistry (WC Protocol)

The following variables are recorded from weekly samplings.

Variable	Units	Precision of recording
Site Identification Code		
Core Measurement Code		
Location Code		
Sampling date		
Sampling time	GMT 24-h clock	1 min
pH	pH scale	0.1
Conductivity	$\mu\text{S cm}^{-1}$	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
$\text{PO}_4^{3-}\text{-P}$	mg l^{-1}	3 significant figures
$\text{NH}_4^+\text{-N}$	mg l^{-1}	3 significant figures
Cl^-	mg l^{-1}	3 significant figures
$\text{NO}_3^-\text{-N}$	mg l^{-1}	3 significant figures
$\text{SO}_4^{2-}\text{-S}$	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. An example is provided in Appendix II.