FWC/FWA Protocols

PHYSICAL AND CHEMICAL VARIABLES

Version 1.1 (Dissolved Organic Carbon (DOC) added, Sep 2005)

Aim

Collection of samples from standing and running waters (or automatic recording where appropriate) for the measurement of environmentally important physical variables and for the analysis of cations and anions.

Rationale

The justification for the variables selected for measurement in this ECN protocol for freshwater physical and chemical variables is provided in the Introduction to this volume under the heading “Selection of Variables” (see page 13). In general the variables have been selected because they are expected to indicate the possible causes and consequences of environmental change in the aquatic environment. Aquatic systems can be considered as consisting of a series of 'master variables' common to all freshwaters, changes in which may significantly affect the system as a whole. Other variables are mainly measures of chemical concentrations which are susceptible to changing inputs and to biogeochemical processes; in addition there are biological components of the systems which are dealt with in other protocols.

Method

Variables to be measured and frequency of measurement

A list of the selected variables to be measured at running and standing water sites is provided in Appendix I of this protocol (page 58), together with recommended and minimum frequencies of measurement. Although there are a few exceptions, most of the variables are common to both running and standing water sites but their frequency of measurement is usually greater at the former. It is anticipated that frequency of sampling will, in practice, commonly exceed the specified minimum frequency. Detection limits for the variables are specified in Chapter 3 (pages 98-99). Water level should be recorded at the same time as the sample is taken for chemical analysis.

Sampling – manual (FWC)

Most variables will be determined from analysis of water samples collected and handled by the methods recommended in the ECN protocol (page 49) 'Recommended sampling procedures for water chemistry' which is intended as a Guide to Good Practice. The document deals with containers, their preparation, use, labelling and storage for both running and standing waters in relation to general chemistry, trace metals, trace organics and pesticides. A widely-accepted text is referenced in the FSP protocol as a source document for the principles involved.

Should operational constraints cause any deviations from the procedures recommended in the ECN protocol, sites must send details of such deviations to the CCU.

Where manual methods are used in the field for physical determinations, (ie pH, temperature, conductivity, turbidity, dissolved oxygen), it is essential that procedures are in place for regular calibration of instruments and quality assurance.

Sampling - automatic (FWA)

A number of both commercially available and research instruments may be used at ECN sites for measuring and recording physical variables in both running and standing waters. Variables commonly measured are pH, temperature, conductivity and turbidity. Instruments usually measure at frequent intervals and record summary values at less frequent intervals; hourly summary values will be reported for ECN purposes. Specifications for sensors and their recording parameters should be discussed with the ECN Central Co-ordination Unit before installation.

Instruments will be located centrally in standing waters and at convenient, agreed locations in running waters to coincide as far as possible with other ECN measurements.

Procedures for chemical analysis

Laboratories of organisations participating in ECN already have well-established protocols for chemical analysis which are subject to internal quality control (QC) procedures and are accredited to formal quality assurance (QA) schemes or participate in internal or inter-laboratory checks on quality. It is therefore impractical and unnecessary to prescribe either the methods or instruments to be used for the chemical analysis of water samples. Where laboratories of organisations which intend to participate in ECN can demonstrate similar or equivalent well-established protocols and QC/QA procedures, these will be acceptable. However it is important that participating laboratories report to the CCU the details of intended methods and associated specifications for each determinand.

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APPENDIX I. Physical and chemical variables

Variable	Recording frequency[1] Running waters[2] Recommended	Minimum	Standing waters[2] Recommended	Minimum
Water level	W	M	F	Q
pH[3]	H	M	H	Q
Suspended solids[4]:				
Dry weight	W	M	F	Q
Ash-free dry weight	W	M	F	Q
or Turbidity[3]	H	M	H	Q
or Secchi disk	n/a	n/a	F	Q
Temperature[3,5]	H	M	H	Q
Conductivity[3]	H	M	H	Q
Dissolved oxygen[5]	W	M	F	Q
Ammonium: NH_4–N	W	M	F	Q
Total nitrogen[6]	W	M	F	Q
Nitrate: NO_3–N	W	M	F	Q
Nitrite: NO_2–N	W	M	F	Q
Alkalinity ($CaCO_3$)	W	M	F	Q
Chloride	W	M	F	Q
Total Organic carbon[6]	n/a	n/a	F	Q
Dissolved Organic carbon	W	M	F	Q
Particulate Organic Carbon	n/a	n/a	F	Q
Biological Oxygen Demand	W	M	n/a	n/a
Total phosphorus[6]	W	M	F	Q
Particulate phosphorus	W	M	F	Q
Phosphate (soluble reactive): PO_4–P				
Silicate: SiO_2	W	M	F	Q
Sulphate: SO_4–S	W	M	F	Q
Sodium – dissolved	W	M	F	Q
Sodium – total[6]	W	M	F	Q
Potassium – dissolved	W	M	F	Q
Potassium – total[6]	W	M	F	Q
Calcium – dissolved	W	M	F	Q
Calcium – total[6]	W	M	F	Q
Magnesium – dissolved	W	M	F	Q
Magnesium – total[6]	W	M	F	Q
Aluminium – labile[7]	W	M	F	Q
Aluminium – total[6]	W	M	F	Q
Tin – dissolved	W	M	n/a	n/a
Tin – total[6]	W	M	n/a	n/a
Manganese – dissolved	W	M	F	Q
Manganese – total[6]	W	M	F	Q
Iron – dissolved	W	M	F	Q
Iron – total[6]	W	M	F	Q
Vanadium – dissolved	W	M	n/a	n/a
Vanadium – total[6]	W	M	n/a	n/a
Nickel – dissolved	W	M	n/a	n/a
Nickel – total[6]	W	M	n/a	n/a
Mercury – dissolved	W	M	n/a	n/a
Mercury – total[6]	W	M	n/a	n/a
Copper – dissolved	W	M	n/a	n/a
Copper – total[6]	W	M	n/a	n/a
Zinc – dissolved	W	M	n/a	n/a
Zinc – total[6]	W	M	n/a	n/a
Cadmium – dissolved	W	M	n/a	n/a
Cadmium – total[6]	W	M	n/a	n/a
Lead – dissolved	W	M	F	Q
Lead – total[6]	W	M	F	Q

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Arsenic – total[6]	W	M	F	Q

Notes

1. Recording frequency abbreviations:
   H hourly
   W weekly
   F fortnightly
   M monthly
   Q quarterly
   n/a not applicable

2. 'Standing water' and 'running water' are used in the text as generic terms to cover more local usage such as broad, lake, loch, lough, and river, brook, beck, burn, stream, respectively. Occasionally, the generic and local terms are used interchangeably

3. Automatic (continuous) monitoring of pH, temperature, turbidity and conductivity should be implemented where possible. Conductivity should be measured (or compensated for) at 25°C. pH should be measured (or compensated for) at 20°C.

4. Suspended solids: dry weight should be determined at 105°±5°C and ash-free dry weight should be determined at 500°±20°C.

5. Standing water profiles: temperature and dissolved oxygen should be monitored at depths appropriate to the standing water site, and the selected depths reported to the ECN Data Manager.

6. 'Total' implies analysis of the <u>un</u>filtered sample.

7. Labile aluminium should only be measured at sites where there is a record of pH ever having been less than 5.5.

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Specification of results and recording conventions

The measurement variables listed below are those required for each FWC or FWA 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. R10)	Unique code for each ECN Site
• Core Measurement Code (e.g. FWC)	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. FWC 01, FWC 02 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: Freshwater physical and chemical measurements – manual sampling (FWC protocol)

The following variables are recorded at a recommended frequency of weekly for rivers and fortnightly for lakes.

Measurement Variable	Determinand code	Units	Reporting precision	Recommended limit of detection(2)
Site Identification Code				
Core Measurement Code				
Location Code				
Sampling Date				
Sampling Time		GMT (24-h)		
Water level		m	0.001	
pH(3) level	PH	pH scale	0.01	
Suspended solids(4)				
Dry weight:	SUSS	mg l^{-1}	3 sig. figs.	2 mg l^{-1}
Ash-free dry weight:	SUSSAF	mg l^{-1}	3 sig. figs.	2 mg l^{-1}
Turbidity(5)	TURB	NTU	0.01	
(L)Secchi disk(5)	SECCI	m	0.1	
Temperature(6)	TEMP	°C	0.1	
Conductivity(7)	CONDY	µS cm^{-1}	3 sig. figs.	1 µS cm^{-1}
Dissolved Oxygen(6)	DISOX	mg l^{-1}	3 sig. figs.	0.1 mg l^{-1}
Ammonium: NH_4–N	NH4N	mg l^{-1}	3 sig. figs.	0.01 mg l^{-1}
Total Nitrogen	NTOT	mg l^{-1}	3 sig. figs.	0.01 mg l^{-1}
Nitrate: NO_3–N	NO3N	mg l^{-1}	3 sig. figs.	0.01 mg l^{-1}
Nitrite: NO_2–N	NO2N	mg l^{-1}	3 sig. figs.	0.01 mg l^{-1}
Alkalinity ($CaCO_3$)	ALKY	mg l^{-1}	3 sig. figs.	0.02 mg l^{-1}
Chloride	CL	mg l^{-1}	3 sig. figs.	0.05 mg l^{-1}
(L)Total Organic Carbon	CTOT	mg l^{-1}	3 sig. figs.	0.1 mg l^{-1}
Dissolved Organic Carbon	DOC	mg l^{-1}	3 sig. figs.	0.1 mg l^{-1}
(L)Particulate Organic Carbon	CPART	mg l^{-1}	3 sig. figs.	0.1 mg l^{-1}
(R)Biological Oxygen Demand	BOD	mg l^{-1}	3 sig. figs.	1 mg l^{-1}
Total Phosphorus	PTOT	mg l^{-1}	3 sig. figs.	0.005 mg l^{-1}
Particulate Phosphorus	PPART	mg l^{-1}	3 sig. figs.	0.005 mg l^{-1}
Phosphate (soluble	PO4P	mg l^{-1}	3 sig. figs.	0.005 mg l^{-1}

reactive):PO_4–P				
Silicate: SiO_2	SIO2	mg l^{-1}	3 sig. figs.	0.01mg l^{-1}
Sulphate: SO_4–S	SO4S	mg l^{-1}	3 sig. figs.	0.005 mg l^{-1}
Sodium – dissolved	NADIS	mg l^{-1}	3 sig. figs.	0.01mg l^{-1}
Sodium – total[8]	NATOT	mg l^{-1}	3 sig. figs.	0.01mg l^{-1}
Potassium – dissolved	KDIS	mg l^{-1}	3 sig. figs.	0.01mg l^{-1}
Potassium – total[8]	KTOT	mg l^{-1}	3 sig. figs.	0.01mg l^{-1}
Calcium – dissolved	CADIS	mg l^{-1}	3 sig. figs.	0.01mg l^{-1}
Calcium – total[8]	CATOT	mg l^{-1}	3 sig. figs.	0.01mg l^{-1}
Magnesium – dissolved	MGDIS	mg l^{-1}	3 sig. figs.	0.01mg l^{-1}
Magnesium – total[8]	MGTOT	mg l^{-1}	3 sig. figs.	0.01mg l^{-1}
Aluminium – total[8]	ALTOT	µg l^{-1}	3 sig. figs.	10 µg l^{-1}
Aluminium – labile[9]	ALLAB	µg l^{-1}	3 sig. figs.	10 µg l^{-1}
(R)Tin – dissolved	SNDIS	µg l^{-1}	3 sig. figs.	1 µg l^{-1}
(R)Tin – total[8]	SNTOT	µg l^{-1}	3 sig. figs.	1 µg l^{-1}
Manganese – dissolved	MNDIS	µg l^{-1}	3 sig. figs.	50 µg l^{-1}
Manganese – total[8]	MNTOT	µg l^{-1}	3 sig. figs.	50 µg l^{-1}
Iron – dissolved	FEDIS	µg l^{-1}	3 sig. figs.	50 µg l^{-1}
Iron – total[8]	FETOT	µg l^{-1}	3 sig. figs.	50 µg l^{-1}
(R)Vanadium – dissolved	VDIS	µg l^{-1}	3 sig. figs.	4 µg l^{-1}
(R)Vanadium – total[8]	VTOT	µg l^{-1}	3 sig. figs.	4 µg l^{-1}
(R)Nickel – dissolved	NIDIS	µg l^{-1}	3 sig. figs.	1 µg l^{-1}
(R)Nickel – total[8]	NITOT	µg l^{-1}	3 sig. figs.	1 µg l^{-1}
(R)Mercury – dissolved	HGDIS	µg l^{-1}	3 sig. figs.	0.1 µg l^{-1}
(R)Mercury – total[8]	HGTOT	µg l^{-1}	3 sig. figs.	0.1 µg l^{-1}
(R)Copper – dissolved	CUDIS	µg l^{-1}	3 sig. figs.	1 µg l^{-1}
(R)Copper – total[8]	CUTOT	µg l^{-1}	3 sig. figs.	1 µg l^{-1}
(R)Zinc – dissolved	ZNDIS	µg l^{-1}	3 sig. figs.	2 µg l^{-1}
(R)Zinc – total[8]	ZNTOT	µg l^{-1}	3 sig. figs.	2 µg l^{-1}
(R)Cadmium – dissolved	CDDIS	µg l^{-1}	3 sig. figs.	0.1 µg l^{-1}
(R)Cadmium – total[8]	CDTOT	µg l^{-1}	3 sig. figs.	0.1 µg l^{-1}
Lead – dissolved	PBDIS	µg l^{-1}	3 sig. figs.	1 µg l^{-1}
Lead – total[8]	PBTOT	µg l^{-1}	3 sig. figs.	1 µg l^{-1}
Arsenic – total[8]	ASTOT	µg l^{-1}	3 sig. figs.	10 µg l^{-1}
For each determinand:				
Laboratory Code[10]				
Limit of Detection Code[11]		character code (<)		
Analysis Date				

Notes

The prefixes (R) and (L) before the determinand names above indicate that the analysis is to be performed for rivers only or lakes only, respectively. Where no prefix occurs, the determinand applies to both rivers and lakes.

(1) These codes should be used within the analytical dataset exactly as given in the Table above. Any additional determinands to be included may be allocated codes by agreement with the ECN Data Manager.

(2) These limits of detection are those recommended by the ECN Statistical and Technical Advisory Group as necessary for the detection of environmental change in the listed determinands.

(3) pH should be measured (or compensated for) at 20°C.

(4) Suspended Solids: Dry weight should be determined at 105°C ±5° and ash-free dry weight should be determined at 500°C ±20°.

(5) Turbidity and Secchi disc are alternatives to Suspended Solids.

(6) Lake profiles: Temperature and Dissolved Oxygen should be recorded at depths considered appropriate to the profile of each particular lake. Information about recording depths should be provided and a numeric suffix to the TEMP and DISOX determinand codes (eg TEMP1, TEMP2, etc) used to identify each depth position.

(7) Conductivity should be measured (or compensated for) at 25°C.

(8) Please note that 'total' implies analysis of the unfiltered sample. If the laboratory routinely filters samples and can only provide 'total dissolved', then the code xxTOTD,

where xx is the symbol for the metal, should be used. For example: ALTOTD for total dissolved Aluminium.

(9) Labile Aluminium should only be measured at sites where there is a record of the pH ever having been less than 5.5.

(10) The Laboratory Code provides the link with the laboratory methods information (see below) to be supplied by freshwater organisations for each of their laboratories. The code should incorporate the organisation acronym where possible and should be agreed the ECN Data Manager.

(11) Where the value of a particular determinand falls below the limit of detection (LOD) for the method, the value of the determinand should be given as the LOD value, and the LOD code set to the character <. Where the value is at or above the detection limit this code should be left null.

Laboratory methods information

Details of analytical methods used by each laboratory involved in ECN should be submitted to the ECN Data Manager. The information is stored in the ECN meta-database and linked with the data *via* the Laboratory Code, Determinand Code and Date range. When any details change, a new record should be submitted by the laboratory and will be added to the database. Aspects of the analysis such as instrument maintenance, calibration, drift, and training of staff will be under the control of the laboratory. The text format for submitting methods information is illustrated below, using nitrate as an example:

Organisation	NERC
Laboratory	ITE, Merlewood
Laboratory Code[1]	ITE-ME
Substance determined	Nitrate
Determinand code	NO3N
Basis of the method	Chemically Suppressed Ion Chromatography
Types of sample	Stream water (FWC)
Typical concentrations	FWC: 0.50
Volume for analysis	10 ml
Calibration range	0.01 to 10 mg l^{-1} – slight deviation from linearity corrected for by using 3rd-order regression.
Method of measurement	Peak area using integration/data system.
Results reported	3 sig figs as N(mg l^{-1})
Detection limit[2]	0.01 mg l^{-1}
Within batch std. devn. (mid range)[3]	2% rsd
Interferences	None
Internal QC measure	CUSUM quality control chart
Accuracy measure	AQUACHECK
Method	Dionex 2002i ion chromatograph with 50 µl injection loop, auto-sampler and sample load pump. Columns –AG4A–SC & AS4A operated with an anion micro-membrane suppressor and using an eluent mixture of 0.15 mM $NaHCO_3$ /2mM Na_2CO_3 at 1.8 ml min^{-1}
Reference	Merlewood Lab method 3.7.5
Method used from date	11-NOV-1992 (the date on which analysis commenced using this method)
Method used until date	(the final date on which this analysis was used – leave blank if current)

Notes

(1) The Laboratory Code should incorporate the organisation acronym where possible. A code should be agreed with the ECN Data Manager.

(2) The detection limit is defined as 4.65 within-batch standard deviation of the blank or a solution with a concentration close to the blank when no signal is detectable from the blank (n = 10).

(3) A within-batch standard deviation in excess of 5% is unlikely to be acceptable.

Core measurement: Freshwater physical and chemical measurements – automatic sampling (FWA protocol)

The following variables are recorded automatically every hour:

Variable	Units	Precision of recording
Site Identification Code		
Core Measurement Code		
Location Code		
Recording (Sampling) date		
Recording (Sampling) time	GMT 24-h clock	1 min
pH (average)	pH units	0.1
Temperature (average)	°C	0.1
Conductivity (average)	$\mu S\ cm^{-1}$	0.1
Turbidity	NTU	1