PC Protocol

PRECIPITATION CHEMISTRY

Version 1.1 **(supplier contact details updated July 2005)**

Aim

To measure the chemical composition of precipitation and dry deposition (bulk precipitation) at ECN sites using a continuously open gauge

Rationale

Although acid rain and its effects have been of interest for more than 100 years (Smith 1872), most high-quality, systematic studies of acidic deposition have been carried out since the 1970s when observations of freshwater acidification alerted scientists to the need for better and more widespread data.

Subsequent research has highlighted the many impacts which the deposition of atmospherically transported pollutants has on ecosystems (eg Last & Watling 1991). The extent and significance of these impacts on physical, chemical and biotic components of ecosystems are likely to be affected by future changes in emissions of pollutants, and make the measurement of the deposition of atmospherically transported material an important activity for ECN. Deposition from the atmosphere has two components - wet deposition consisting of rainfall or snowfall, and dry deposition consisting of gaseous and particulate material. Dry deposition of pollutants can be calculated for some components as the difference between their concentrations in a continuously open collector and in a collector which is open only during precipitation episodes. It can also be calculated from the concentrations of gaseous and particulate pollutants and of deposition velocities. The use of a continuously open funnel (bulk collector) results in the collection of both dry and wet deposition and, although there are advantages to be gained from separating the two sources of input, it was concluded that only bulk deposition would be measured in ECN on the grounds of the considerable additional costs attaching to the separate measurement of the components.

The main source of data on the geographical distribution of deposition in the UK has been the United Kingdom Precipitation Composition Network, operated until recently by the Warren Spring Laboratory on behalf of the Department of the Environment (Review Group on Acid Rain 1990). The methods used in this Protocol conform with those used at Secondary Sites of the UK Precipitation Composition Monitoring Networks (UKPCMN) described in Devenish (1986). This allows results from ECN sites to be linked with the 32 rural UKPCMN sites at which monitoring started in 1986.

Method

Equipment

The bulk collector is constructed to the design described by Hall (1986). It consists of a conical polythene funnel which rests on the neck of a polythene collecting bottle. Two funnel sizes are available, each with a 63° cone; the smaller has a diameter of 115 mm, whilst the larger has a diameter of 152 mm and is likely to be appropriate at all ECN sites. The upper surface of the collector is 1.75 m above the ground. A removable filter of 1 mm mesh Teflon prevents coarse debris from falling into the collecting bottle which is surrounded by a jacket of polished steel, from the collecting bottle, from which it is separated by a 25 mm gap. The sample is kept dark and cool by the jacket. The collector has a bird deterrent but this is not always successful and may need to be supplemented by setting up alternative, decoy bird perches some distance from the collector. Details of the required equipment are provided in Appendix II.

Location

Local sources of contamination should be avoided, or their effects minimised, by placing the collector upwind of any such sources. Proximity to vehicle tracks

which may become dusty in dry weather, and to animal houses, should be avoided. The collector should be placed in an open location well away from obstructions such as buildings and trees, adjacent to the TSS and as near as is practicable to the soil solution samplers, but it should be borne in mind that regular visits to the collector are likely to cause trampling of vegetation and compaction of the soil. An acceptable alternative location is close to the weather station but each instrument should not cause an obstruction to the other. The collector must be either bolted to a concrete base or secured by guy ropes.

Sampling

The procedure to be used in collecting samples is described in Appendix I, and follows closely the procedures adopted by the Warren Spring Laboratory. Whenever possible the collection bottle should be changed at the same time and on the same day each week; the standard which has been adopted for ECN is Wednesdays at 0900 GMT. The bottle containing the precipitation is removed and is replaced by a clean bottle fitted with a clean filter. The funnel is either cleaned with de-ionised or distilled water and shaken to remove droplets, or is replaced by a funnel which has been cleaned in the laboratory. A funnel containing ice or snow at the time of sample collection must be transferred to the new bottle without having been cleaned or replaced; the ice and snow are thus left to melt into the new bottle when weather conditions permit.

The bottle and its contents are returned to the laboratory, where the volume of precipitation is determined to the nearest 1 ml. To determine the volume, the bottle (without cap) and its contents are weighed and the weight of the dry bottle subtracted to give the weight of contents. Conductivity and pH are measured on unfiltered water according to methods provided in the ECN Initial Water Handling (WH) Protocol which also sets out procedures for filtering 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 and alkalinity. In calculating fluxes, precipitation volume should be taken from the nearby automatic weather station or standard rainguage because the bulk precipitation collector may give less accurate volume estimates, eg after snow has fallen.

Labelling

Each water sample is identified uniquely by:

- the ECN Measurement Code (PC),
- 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. The recording form for this measurement includes codes for factors which potentially affect the chemistry of the sample, such as the presence of insects, dust, or bird droppings in the funnel or bottle, as well as local disturbances such as fires, dust sources, etc.

Washing equipment

Laboratory washing of the funnel, filter and bottle should be carried out with a laboratory cleaning agent, as described for bottle washing in the ECN Initial Water Handling (WH) Protocol.

Quality assurance

QA procedures will follow those adopted for the Acid Deposition Monitoring Network (Heyes, Irwin & Barrett 1985). These include assessment of errors which may be introduced during sampling, sample handling and analysis.

Authors

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References

Devenish, M. 1986. *The United Kingdom Precipitation Composition Monitoring Networks.* Stevenage: Warren Spring Laboratory.

Hall, D.J. 1986. *The precipitation collector for use in the Secondary National Acid Deposition Network.* Stevenage: Warren Spring Laboratory.

Heyes, C.J., Irwin, J.G. & Barrett, C.F. 1985. Acid deposition monitoring networks in the United Kingdom. In: *Advancements in air pollution monitoring equipment and procedures*, 155-168. Bonn: Federal Ministry of the Interior.

Last, F.T. & Watling, R., eds. 1991. *Acidic deposition, its nature and impacts.* Edinburgh: Royal Society of Edinburgh.

Review Group on Acid Rain. 1990. *Acidic deposition in the United Kingdom 1986-1988.* London: Department of the Environment.

Smith, R.A. 1872. *Air and rain. The beginnings of a chemical climatology.* London: Longmans, Green & Co.

Appendix I. Routine sample collection

Materials

- A clean sample bottle with a screw cap attached. The sample code and the dry weight of the bottle without cap should be marked on the bottle with a water-resistant felt pen
- A wash bottle containing de-ionised or distilled water (DW)
- Forceps
- Two clean funnel filters (in case of one being dropped) in separate, sealed polythene bags
- Two clean funnels (in case of one being dropped) in separate sealed polythene bags
- A clean bottle cap in a sealed polythene bag
- An empty clean polythene bag large enough to contain the funnel assembly during bottle changing
- Field recording form and pencil

Procedure

1. Note any obvious signs of bird droppings, dust, smuts, or any other unusual occurrences or disturbances on the field recording form using appropriate codes, or text if suitable codes do not exist.

2. Detach the funnel assembly from the sample bottle. First unclip the retaining springs, then hold the stem of the funnel and pull it upwards whilst easing the lower end out of the bottle with the other hand. Do not put your fingers inside the top of the bird guard. Be careful not to tip out the funnel insert. Place the funnel and the filter insert inside the polythene bag whilst you deal with the sample bottle.

3. Take the clean cap from the polythene bag and screw it very firmly on to the sample bottle. Be careful to prevent anything entering the bottle and avoid especially the possibility of contamination from your fingers round the neck and rim of the bottle.

4. Remove the sample bottle. The bottle should be raised far enough to allow it to pass sideways between two of the struts supporting the bird guard rings.

5. Insert the clean sample bottle complete with its screw cap. It should be inserted sideways between two of the struts holding the bird guard rings, and then lowered into the inner metal container. Leave the screw cap in position.

6. Remove the filter insert from the funnel with forceps and leave it in the polythene bag.

7. If there is no evidence of significant contamination to the funnel (eg bird droppings), wash the funnel assembly by flushing with DW. Vigorously shake off the excess water and do not use paper tissues. If there is evidence of significant contamination, or if the funnel has not been washed in the laboratory for six weeks, it should be replaced with a clean funnel. A clean filter insert should be used each week.

8. The screw cap should now be removed from the new bottle and placed in a polythene bag for use on the next visit to the collector.

9. Insert the funnel vertically through the bird guard and position the lower end firmly in the bottle. Attach the retaining clips.

10. Check that the top of the funnel is horizontal.

11. It is **VITAL** to check that the cap is screwed down very firmly on the bottle containing the sample, so that leakage cannot occur during its transport to the laboratory.

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Appendix II. Equipment details

Materials

- Complete assembly: aluminium stand, bottle holder, reflector, funnel retainer assembly, polythene catchment funnel assembly, filter and catchment bottle
- Spares: funnel assembly catchment bottle filter

It is recommended that three funnel assemblies, bottles and filters should be available for each site.

Funnel size (usually 152 mm and not 115 mm) should be specified.

Supplier

Just Plastics Ltd — Sole supplier (as far as is known)
The Maltings
Weyford Bridge
Stalham
Norwich — *Tel: 01692 581 000*
Norfolk NR12 9LL, UK — *Fax: 01692 581 848*

Specification of results and recording conventions

The measurement variables listed below are those required for each PC 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: precipitation chemistry (PC Protocol)

The following variables are recorded weekly.

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
Volume	ml	1
pH	pH scale	0.1
Conductivity	µS 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

Recording forms
A standard field recording form is available from the CCU.

Note
[1] Date/time bottle last emptied and set out