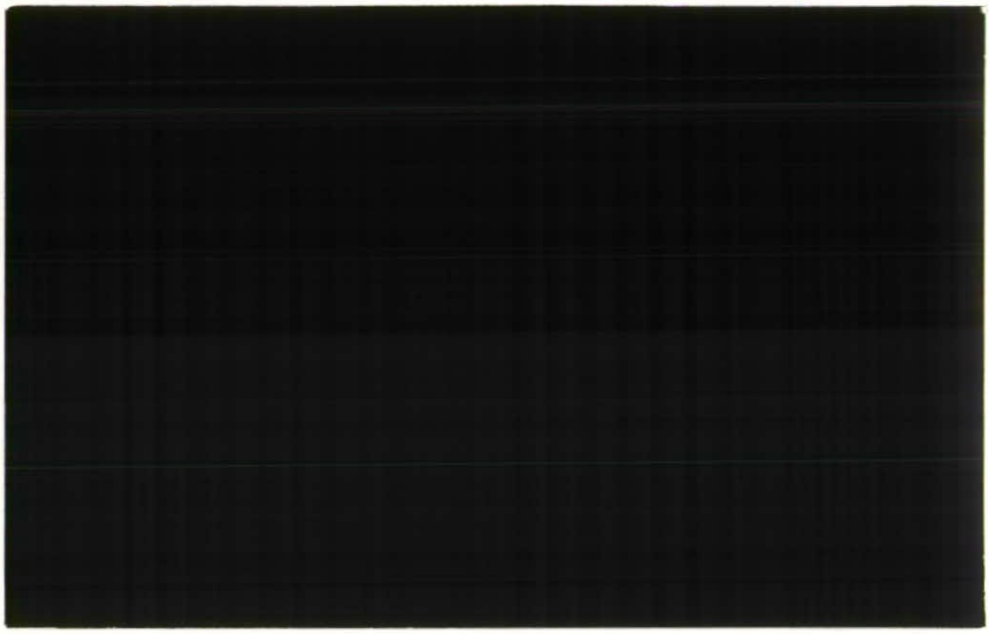
Institute of Hydrology



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VOLUME I

APPENDICES 1

APPENDIX 1 - Ciba Agriculture protocol and amendments

CIBA AGRICULTURE

RESEARCH AND DEVELOPMENT

ANALYTICAL STUDY PROTOCOL

Project No: CSTR 011/8

Date: November 1992

DETERMINATION OF CGA 131036 RESIDUES OCCURRING IN DITCH WATER AFTER AN APPLICATION OF LOGRAN 20 WG AT 37.5 g/ha.

PROTOCOL AUDITED BY: .....

Mr D Barratt BScHons, MRSC, CChem
Environmental Health and Safety Manager
CIBA-GEIGY Agriculture, Whittlesford,
Cambridge

STUDY DIRECTOR : .....

Mr T Tack BA, LRSC
Head of Residue Section,
CIBA-GEIGY Agriculture, Whittlesford,
Cambridge

APPROVED BY SPONSOR: .....

Mr T G Marks BSc, Dip Agric, DTA,
MIBiol, C Biol
Registration Manager
CIBA-GEIGY Agriculture, Whittlesford,
Cambridge

1 OBJECTIVE

To monitor potential residues of Triasulfuron (CGA 131036) which may occur in streams and ditches via water drainage after rainfall events following use of LOGRAN 20 WG according to good agricultural practice.

This data is required by Pesticide Safety Division (PSD) to assess the risk of contamination to streams and ditches from water drainage by CGA 131036 applied as LOGRAN 20 WG.

2 BACKGROUND

See notice of approval letter 0526 of 1992 ex Ministry of Agriculture, Fisheries and Food Pesticide Safety Division section 4 ix (Appendix 1).

3 SITE DETAILS

The study will be conducted at ROSEMAUND EHF, Herefordshire under the supervision of staff from 'ADAS Rosemaund Managment Group' and CIBA Agriculture utilising equipment installed on the site to sample water either automatically or by hand (Ref 1) after a rainfall event.

4 APPLICATION DETAILS

LOGRAN 20 WG (Batch number to be recorded) will be applied to part of the field Stoney and Brushes and all of the fields Foxbridge and Longlands, an area of approximately 12 ha of winter wheat at 37.5 g/ha.

The date of the application will be approximately 01.02.93 (date and time to be recorded).

No application will be made to areas identified by Rosemaund EHF as used for demonstration to third parties.

The application will be made according to Good Agricultural Practice.

If no rainfall event(s) are recorded 28 days after the first application at the discretion of the Study Director and the agreement of the ADAS Rosemaund Managment Group a second application of LOGRAN 20 WG will be made to the field name ..oorfield, an area of approximately 9 ha at 37.5 g/ha. (Full details will be identified by protocol amendment).

100ml of spray liquor will be removed from the spray tank before and after application and stored at -18 °C until analysis. The sample(s) will be labelled with date, time of sampling and project number.

5 CULTIVATION DETAILS AND SITE HISTORY

Full details of soil structure, previous husbandry practices and application details will be supplied by ADAS Rosemaund Managment Group.

Full details of drainage plans will be supplied in the final report.

6 SAMPLING DETAILS WATER

a) Sampling Points

The sampling points as outlined in Ref 1 and summarised below will be used.

A map of all sampling points will be supplied in the final report.

Rosemaund descriptive name	CIBA Agriculture reference
Moorfield (MAFF)	011/8/A
Upper Drain site 5 (MAFF + IH)	011/8/B
Upper Gauging site 1 (MAFF)	011/8/C
Drain site 3 (MAFF)	011/8/D

b) Sampling times

i) 1000ml samples of water will be taken from each sampling point not more than 14 days before application and uniquely labelled as in 6d.

100ml of spray liquor will be removed from the spray tank before and after application and stored at -18 °C until analysis. The sample(s) will be labelled with date, time of sampling and project number.

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6 SAMPLING DETAILS WATER

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The sampling points as outlined in Ref 1 and summarised below will be used.

A map of all sampling points will be supplied in the final report.

Rosemaund descriptive name	CIBA Agriculture reference
Moorfield (MAFF)	011/8/A
Upper Drain site 5 (MAFF + IH)	011/8/B
Upper Gauging site 1 (MAFF)	011/8/C
Drain site 3 (MAFF)	011/8/D

b) Sampling times

i) 1000ml samples of water will be taken from each sampling point not more than 14 days before application and uniquely labelled as in 6d.

ii) 1000ml of water will be taken automatically from sampling points 011/8/B, 011/8/C and 011/8D after each rainfall event following application of LOGRAN 20 WG using automatic samplers developed at Rosemaund EHF, each sample taken will be uniquely labelled as in 6d.

iii) No water samples will be taken >120 days after application unless at the specific request of the Study Director.

iv) Extra samples may be taken at the request of the Study Director. All details of extra samples will be recorded by the Study Director and ADAS Rosemaund Managment Group.

v) At each automatic sampling one sample will be provided every hour up to 12 hours and then every 3 hours to 24 hours (16 samples). Extra samples may be taken at the discretion of ADAS depending on the rainfall event using Telemetry developed at ADAS Rosemaund Managment Group.

c) Sample containers

All sample storage containers will be glass.

d) Sample labelling

Sample time DAA	Sample points CIBA Ref. No.	Sample label
* =-14	011/8/A	011/8/A/1
	011/8/B	011/8/B/1
	011/8/C	011/8/C/1
	011/8/D	011/8/D/1
* At first rainfall event (n = 2)	011/8/B	011/8/B/2/DAA/TIME
	011/8/C	011/8/C/2/DAA/TIME
	011/8/D	011/8/D/2/DAA/TIME
* At n rainfall event (n + 1)	011/8/B	011/8/B/n+1/DAA/TIME
	011/8/C	011/8/C/n+1/DAA/TIME
	011/8/D	011/8/D/n+1/DAA/TIME

Where DAA = DAYS after application
TIME = Time sample taken

* If sample not taken then reason to be recorded.

c) Sample storage

After sampling each sample will be transferred by carrier to the laboratory (to be identified later) within 24 hours. If transportation cannot be made within 24 hours all samples will be stored at -18 °C until sample transfer. (All bottles will be laid on their sides to minimise sample expansion on storage).

The temperature of the storage system will be monitored regularly.

7 WEATHER AND HYDROLOGY DATA

All weather and hydrology data will be recorded on the Rosemaund EHF site and attached as an appendix to the final report.

8 ANALYTICAL DETAILS

(i) The overall study (as defined in the title) will be undertaken to the principles of GLP.

ii) Test substances

LOGRAN 20 WG	Batch number	To be recorded
	Certificate of Analysis	To be issued by Analytical Manager CIBA Agriculture, Whittlesford

Analytical reference standard

Batch number)	
Purity)	To be recorded
Expiry date)	

Certificate of analysis and spectral details will be issued with the final report.

iii) Method of analysis REM 116.02 will be validated capable of determining residues of CGA 131036 to 0.01 µg/l.

Analytical data should support a method validation statement to show procedural recoveries of;

≈ 0.02 µg/l
≈ 0.15 µg/l
≈ 1µg/l

for CGA 131036 in water.

The pH of samples will be recorded during analysis.

The method will provide analytical data for the final report and will include the following information,

a) full experimental details
b) details of method validation
c) full experimental procedures
d) typical validation chromatograms to support the above data.

iv) The study director will receive a typed report. The report will include the following information;

a) summary of analytical results
b) summary of validated method
c) summary of sample history
d) analytical results and method validation
e) typical examples of chromatography including

- a typical standard chromatogram for all compounds.
- a typical method validation chromatogram for CGA 131036 in water.
- a typical untreated water chromatogram.
- a typical sample water chromatogram after a rainfall event.

v) Attached as an appendix to the report will be;

- A copy of the validated method of analysis.
- Full spectral details confirming the ID of the analytical reference standard.
- Certificate of analysis for the analytical reference standard and batch number of product applied.

9 TERMINATION OF THE STUDY

If residues of triasulfuron are <0.01 µg/l after a minimum of 2 rainfall events or adverse weather considerations are influencing the study the Study Director will, after discussion with ADAS Rosemaund Managment Group, recommend the study be terminated and the Sponsor notified.

10 DISCUSSION OF ANALYTICAL RESULTS

All samples will be analysed within 10 days of receipt by the laboratory and all results will be communicated to the Study Director.

All results will be communicated to the ADAS Rosemaund Managment Group for discussion with the Study Director.

11 COLLATION OF RESULTS

After termination of the study all results will be collated by the ADAS Rosemaund Managment Group and interpreted with weather data and hydrology data supplied on site. A complete report on the study will be forwarded to the Study Director for discussion.

12 QUALITY ASSURANCE

Quality Assurance (QA) will be arranged by D J Barratt.

13 ARCHIVING

The original final report and raw data (supported by a QA statement) will be collated by the Study Director and sent to archive for storage (SOP GLPRA).

The Archive is located in Room No 28 and named GLP Archive.

14 STUDY PERSONNEL

CIBA Agriculture Personnel

T G Marks	Registration Manager CIBA Agriculture (Sponsor)
T Tack	Residue Chemistry Manager CIBA Agriculture (Study director)
P Ryan	Herbicide Development Manager

ADAS Rosemaund Management Group to include:

Steven Baily	BSc (Hons), MAGRST	(ADAS SWRC)
Graham Harris	BSc (Hons), MPhil	(ADAS SWRC)
Richard Williams	BSc (Hons)	(Institute of Hydrology)
Caroline Hack	BSc (Hons)	(ADAS Rosemaund)
Peter Matthiessen	BSc (Hons), PhD	(MAFF)

15 REFERENCES

1. Pesticide runoff study at Rosemaund EHF Autumn 1987 - 1990.

2. ADAS Specification Document 011/8.Spec.

REASON

To update protocol to reflect changes in field application procedures and the location of the laboratory to analyse water samples.

4. APPLICATION DETAILS

The application will be made according to Good Agricultural Practice and reflect approved label recommendations.

8. ANALYTICAL DETAILS

i) The laboratory for analysis will be Hazelton (UK) Ltd, Otley Road, Harrogate.

ii) Analytical reference standard

Batch number	:	266/102
Purity	:	99.5 ± 0.2%
Expiry date	:	5/94

iii) Method of analysis REM 116.02 will be modified and validated capable of determining residues of CGA 131036 to 0.01 µg/l.

v) A calculation outlining the limit of determination.

T. Tait
1.2.93.

REASON

To review protocol, especially field application status as no significant rainfall event has been recorded at Rosemaund EHF.

4. APPLICATION DETAILS

LOGRAN 20 WG (batch number to be recorded) will be applied to the field named Longlands at an application rate of 37.5 g/ha.

No application will be made to the field named Moorfield.

6 SAMPLING DETAILS

a) Before application to Longlands, soil samples to a depth of 10cm, a minimum of 10 samples to be collected individually. No bulking of sample should be undertaken.

- Soil samples taken before application and within 24 hours after application.
- Volume of soil corer to be recorded.
- Samples to be taken in a W shaped profile across the field and position recorded.

b) Samples before application to be labelled LONG/1/n where n = sample number

Samples after application to be labelled LONG/2/n where n = sample number

All samples to be stored at -18 °C before shipment to Ciba Agriculture, Cambridge.

c) All soil samples to be analysed with reference to method REM 116.11.

14 STUDY PERSONNEL

Sponsor
Study Director
Herbicide Development Manager
ADAS Rosemaund Management Group
Quality Assurance
PSD (Dr Andrew Craven)

30.4.93

REASON

To review site history of field study following communication between T Tack (CA) and G Harris (ADAS).

APPLICATION SITE DETAILS

Due to negligible rainfall at Rosemaund and subsequent discussion between CA/ADAS/PSD it was agreed to overspray Longlands before an imminent rainfall event if possible at recommended label rate'

Date of application 31.03.93 to Foxbridge and Longlands (in error).

SAMPLING DETAILS

Water samples - see local records and transported to Hazelton UK (HUK).

Soil samples - 10 soil samples taken from Foxbridge before application to a 10 cm depth.

- 10 soil samples taken from Foxbridge to a 10 cm depth as soon as practical after application.

8 ANALYTICAL DETAILS

Water samples to be analysed at HUK based on protocol number P7910d, agreed between T Tack and M Curl (HUK) dated 07.01.93.

Soil samples will be analysed at CA with reference to REM 116:11.

Method validation to be advised.

14 STUDY PERSONNEL

Sponsor
Study Director
Herbicide Development Manager
ADAS Rosemaund Management Group
Quality Assurance
PSD (Dr Andrew Craven)

T. Tack
30.4.93

REASON

To review labelling of samples received from ADAS Rosemaund as outlined in Protocol Amendment No 3.

8 ANALYTICAL DETAILS

Samples have arrive inconclusively labelled. There are no means of identification to distinguish between sampling dates. Each bag contains 10 subsamples labelled inconclusively.

Each bulked sample will be given a unique reference number under supervision of QA and analysed in duplicate with reference to REM 116:11

On the inference that the subsamples will be of different concentrations, interpretation of results and possible identification of samples will discussed when results are obtainable.

Organic matter, pH and mechanical analysis will also be determined.

Method validation will be determined in triplicate at;

≈ 0.05 mg/kg
≈ 0.10 mg/kg
≈ 0.50 mg/kg

on untreated soil supplied by ADAS Rosemaund (private communication C Hack, 21.05.93).

Interpretation of results

All results will be discussed with ADAS Rosemaund Management Group, Ciba Agriculture, Hazelton UK Limited and other interested personnel, on submission of draft report by G Harris.

14 DISTRIBUTION

Sponsor
Study Director
Herbicide Development Manager
Hazelton UK Limited
ADAS Rosemaund Management Group
Quality Assurance
PSD (Dr Andrew Craven)
Analyst (S Adams)
Archive

APPENDIX 2 - ADAS Contract Specification

CIBA AGRICULTURE - PROJECT NO: CSTR 011/8

ADAS SPECIFICATION DOCUMENT 011/8. Spec.

Experimental Location:	ADAS Rosemaund, Preston Wynne, Hereford
Period of Contract:	1 February 1993 for 120 days maximum

Triasulfuron (CGA 131036)

Work to be undertaken to meet Ciba Agriculture Project No: CSTR 011/8 as specified in Analytical Study Protocol, dated December 1992.

CONTRACT

The contract is between Ciba Agriculture and ADAS Rosemaund. The ADAS work will be undertaken jointly by ADAS Soil & Water Research Centre, Cambridge and ADAS Rosemaund, to the specification detailed below. ADAS will sub-contract part of the the work to the Institute of Hydrology, Wallingford and MAFF Fisheries, Burnham on Crouch. The sub-contracts will be used to provide support data to the study. The above parties will together form the Rosemaund Management Group as specified in the Ciba Agriculture Protocol CSTR 011/8.

SPECIFICATION

Method:

To install four flow related samplers at stations:

Moorfield (ADAS)	011/8/A
Upper drain site 5 (MAFF + IH)	011/8/B
Upper gauging site 1 (MAFF)	011/8/C
Drain site 3 (MAFF)	011/8/D

(a) To record the runoff at each station and monitor rainfall continuously for the period of study (up to 120 days)

(b) To analyse the resultant data and provide a comprehensive report to Ciba Agriculture to meet the objectives specified in the Protocol for Project CSTR 011/8.

ADAS

Approach:

(a) To apply the pesticide - triasulfuron (CGA 131036) using a Chaviot dedicated sprayer (Chaviot 902), 12m boom width. Specification - 1000litre plastic tank, 150litre/min pump.

(b) To continuously record flow rate, at each monitoring station, utilising the in-situ sharp-crested V-notch weirs designed to BS 3680 and by calibrated electronic or similar head recorders.

(c) To install four secure Epic wastewater samplers (1011T), one per station, modified to collect 1000ml water samples in accordance with ADAS SOP DRAIN/018/Draft.

(d) To programme the sampling equipment to meet the agreed sample collection as specified in Ciba Agriculture Protocol CSTR 011/8. This programme will include a flush routine to purge the sampling module collecting vessel with the water to be sampled, immediately prior to sample collection. Each sample will be delivered by a discrete silicon rubber/teflon tube to an individual 'identified' sample bottle.

(e) Samples will be taken in discrete 1000 ml Amber bottles (soda glass - Lewis & Towers) with co-Polymer caps and seals with PTFE inner discs. Each bottle will be as delivered by the manufacturer, unused and despatched to ADAS Rosemaund with dust cap in situ. Caps will be added after sample collection. Sampling tubes will be rinsed in distilled water prior to each use.

(f) In the event of failure of any of the specified EPIC (1101T) samplers, installed specifically to support this study, to take the sample(s) needed to meet the Protocol CSTR 011/8, ADAS will notify Ciba Agriculture on the first working day following this occurrence. Opportunities to utilise alternative comparable samples from ADAS Rosemaund will be examined following discussions between ADAS and Ciba Agriculture.

(g) All relevant field sampling details will be recorded on a protocol form designed specifically for this study. This will include weather details at the time of transfer of samples from the field to the ADAS Rosemaund laboratory. All samples will be labelled and transferred to Ciba Agriculture in accordance with the conditions specified in Protocol Project CSTR 011/8.

(h) ADAS will collect the flow and sampling time data utilising a Campbell Data Logger installed at ADAS Rosemaund, at such time intervals so as to provide a continuous flow record to a minimum of 30 minute intervals and a record of sampling times to within 5 minutes.

(i) To transfer the above data from ADAS Rosemaund to ADAS SWRC, utilising a modem and British Telecom telephone line, and to load this data onto a computer-held database for subsequent interrogation. In the event of failure of the telemetric data transfer for whatever reason, ADAS will provide, within a reasonable period, data to a similar specification by appropriate alternative means.

(j) ADAS will undertake the necessary programming to target the received data and will check and plot the data on a daily/weekly basis, as appropriate, to provide graphs and tables showing flow rates and sampling occasions.

(k) ADAS will calculate flow volumes for each of the four sites and will use this data and sample concentration data for triasulfuron (provided by Ciba Agriculture as defined in the Protocol 011/8) to provide pesticide loads for each specified period.

(l) The Rosemaund Management Group will assess the derived data above and utilise, as appropriate, historical data from the ADAS Rosemaund site to provide a comprehensive report to Ciba Agriculture. This report will meet the requirements of the Protocol for Project No: CSTR 011/8 and will include full details on field data collection and sampling protocols utilised.

(m) A draft report will be provided to Ciba Agriculture within 30 days of the completion of fieldwork and delivery of all necessary and appropriate analytical data and reports. The final report (3 copies) will be delivered to Ciba Agriculture after a period of reasonable consultation between the parties to an agreed deadline.

(n) Payment terms are as specified in the Contract between ADAS and Ciba Agriculture. The contract price of £50k plus VAT will be reduced by 10% if, at the request of Ciba Agriculture, the period of field work or sample numbers are reduced. The full contract will cover a maximum sampling period of 120 days and between 350 and 550 water samplings. However, if a smaller number of samples are taken and/or the sampling/contract period is reduced by at least 50 days, the reduction stated above will apply. In this case the contract price will be £45k plus VAT.

(o) Monthly interim data reports will be provided by ADAS to Ciba Agriculture nominally at the beginning of March, April and May and/or at other mutually agreed and appropriate dates to enable an interaction and dialogue to take place between ADAS and Ciba Agriculture. This will be used to support the decisions to be taken on sampling strategy during the study. Both parties will make due effort to exchange sampling data and advise accordingly.

Robert W. Cox

18 January 1995

APPENDIX 3 - Hydrological site installations

Hydrological Site Installation

011/8/A (Moorfield)

The flow from the catchment at Moorfield was provided by a 0.8m width, 0.4m depth, 90°V-notch sharp-crested weir. This was installed in accordance with ADAS SOP DRAIN/006. The fall in head across the weir plate was designed to be sufficient to avoid water backing up to the plate. The weir plate was designed and installed in accordance with ADAS SOP DRAIN/003. The weir crest was constructed in stainless steel and mounted on to a 6mm steel plate, positioned across the ditch at right angles to the flow. The weir plate was chamfered in accordance with the specification described in BSI 3680 (1981). The head depth over the weir was measured at a location of 4.0m upslope of the weir plate, within the stilling pool of the weir in accordance with BSI (1981). The head water level recorders were installed in accordance with ADAS SOPs DRAIN/011 and DRAIN/024. The SWRC head device was calibrated over the full range (range 300mm, resolution +/- 1mm) using a static calibration tube at Cambridge on (15/02/92) in accordance with ADAS SOP DRAIN/015. The backup capacitive probe (range 1.0m, resolution +/- 5mm) was spot calibrated in accordance with ADAS SOP DRAIN/016/DRAFT. The calibration of the weir was derived from the tabulated charts given in BSI 3680 (1981), extended over the full range of the weir. The maximum capacity of the weir was determined as 139 litres/s, equivalent to a catchment flow of 7.9 mm/h.

011/8/B (Longlands)

The flow from the drain at Longlands was measured in a rectangular blue PVC weir tank, 0.6m long, 0.9m wide and 0.30m depth. The tank was installed in accordance with ADAS SOP DRAIN/004 and was constructed on a metal platform with legs to raise the base of the tank above the maximum depth of flow in the ditch system into which the weir discharged. This ensured free outfall conditions in times of high runoff. The weir crest was rectangular and constructed in stainless steel in accordance with the specification in BSI 3680 (1981). The tank capacity was 9.0 litre/s, equivalent to 1.69 mm/h. A calibration record was determined on 05/12/91 for the full range of the weir tank utilising a Fisher Venturi Flowmeter in-situ laboratory rig at the ADAS SWRC laboratory. The calibration of the rig is checked annually by volumetric spot checks. Full certification of the range of the laboratory calibration rig was provided by Fisher Controls in 1980.

Water entry to the weir tank was baffled at 0.06m from the drainpipe entry point to reduce water turbulence. The head waterlevel recorders

were installed in accordance with ADAS SOP DRAIN/011 with the depth measured at 0.2m from the weir plate. The SWRC waterlevel recorder was calibrated over the full range (range 90mm, resolution +/- 1mm) using a static calibration tube at Cambridge on 05/12/91 in accordance with ADAS SOP DRAIN/015. The back-up capacitive probe (range 0.5m, resolution +/- 2.5mm) was spot calibrated in accordance with ADAS SOP DRAIN/016/DRAFT.

011/8/C (Jubilee)

The flow from the 'permanently' flowing stream in the catchment at Jubilee was provided by a 1.2m width, 0.6m depth, 90°V-notch sharp-crested weir, installed in accordance with ADAS SOP DRAIN/003. The fall in head across the weir crest was designed to be sufficient to allow free fall for the range of the weir. The weir plate was constructed in stainless steel and mounted on to a 6mm steel plate, positioned across the ditch at right angles to the flow. The crest plate conforms with the specification described in BSI 3680 (1981). The head depth over the weir was measured at a location of 0.85m upslope of the weir plate, within the stilling pool of the weir, in accordance with BSI 3680 (1981). The head waterlevel recorders were installed in accordance with ADAS SOP DRAIN/011 and DRAIN 024. The SWRC waterlevel recorder was calibrated in accordance with ADAS SOP DRAIN/015 over the full range (range 1.0m, resolution +/- 1mm) using a static calibration tube at Cambridge on (13/12/92). The capacitive probe (range 2.0m, resolution +/- 10mm) was spot calibrated in accordance with ADAS SOP DRAIN/016/DRAFT. The calibration of the weir was derived from the tabulated charts given in BSI (1981) extended over the full range of the weir. The maximum capacity of the weir was determined as 382 litres/s, equivalent to a catchment flow of 4.49 mm/h.

011/8/D (Foxbridge)

The flow from the drain at Foxbridge was measured in a rectangular glass fibre black weir tank, 1.2m long, 0.30m wide and 1.1m depth. The tank was installed in accordance with ADAS SOP DRAIN/001 and was positioned on a level section of the stream bed, anchored firmly to the concrete outfall inlet drainage pipe. The base of the weir plate was 0.3m above the stream bed to provide free outfall conditions in times of high drainflow. The 1/2 90°V-notch weir crest constructed in stainless steel, in accordance with the specification in BSI 3680 (1981).

The tank capacity was 20 litre/s, equivalent to 1.21 mm/h. A calibration record was determined on 10/01/92 for the full range of the weir tank utilising an in-situ laboratory flow rig at the Cambridge SWRC laboratory. The calibration of the rig is checked annually by

volumetric spot checks. Full certification of the range of the Fisher Vane Flowmeter rig was provided by Fisher Controls in 1980 in 1980.

Water entry to the weir tank was baffled twice at 0.25m and 0.6m from the drainpipe entry point to reduce water turbulence. The head depth was measured at 0.6m from the weir plate. The head waterlevel recorders were installed in accordance with ADAS SOP DRAIN/011 and DRAIN/024. The SWRC waterlevel recorder was calibrated using a static calibration tube at Cambridge in March 1988, over the full range (range 300mm, resolution +/- 1mm) in accordance with ADAS SOP DRAIN/015. The capacitive probe (range 1.0m, resolution +/- 5mm) was spot calibrated in accordance with ADAS SOP DRAIN/016/DRAFT

Water Sampling Equipment

At 011/8/A (Moorfield) the EPIC wastewater sampler (No 16887) was located in a wooden box on a platform adjacent to the weir. At the time of the study this wooden box was located on the northernmost platform upstream of the installations at this site. The sampler was connected by cables directly to the Campbell logger box located on the southernmost platform at 011/8/A (Moorfield). At 011/8/B (Longlands) two EPICS were installed to support the study, α as the main sampler (No 16888), located furthest away from the field. The box nearest the field housed the back-up sampler β (No 16890). Both inlet tubes (see below) extracted water from the same location in the weir tank. The sampler was connected by cables to the logger box, labelled 011/8/B, located in the small hut at station 011/8/C (Jubilee).

At 011/8/C (Jubilee) the sampler (No 16889) was located inside the main site hut. The sampler was connected directly via cables to the datalogger box, labelled 011/8/C, located in the small hut. At 011/8/D (Foxbridge) the sampler (No 16891) was situated in the tall box on the platform. The sampler was connected directly via cables to the datalogger box, labelled 011/8/D, located in the small hut at site 011/8/C (Jubilee)

At all the sampling points, the water sampler entry tubes were sited facing upstream in accordance with ADAS SOP DRAIN/023 in the mid-stream position in both the open ditches and weir tanks. The sampling methodology met the basic conditions specified in BSI 6068 (1991) although tube entry velocity was controlled by the pump rate on the EPIC wastewater sampler and not the velocity of the water being sampled. This was not considered to be a problem as measures were taken to reduce the velocity of water at the sampling point by use of the baffles in the weir tanks and the stilling pools in the ditches.

Sampling procedures

The sampling programme routine adopted was described in the ADAS Specification Document 011/8. The pre-set EPIC wastewater sampler routine controlling the collection of individual water samples was set up in accordance with ADAS SOP DRAIN/019. In order to allow for a number of options once sampling had been initiated, the sophisticated datalogger programme assessed the water level at each site individually at regular intervals and would cancel (abort) the routine after four samples (hourly) if the water level had not continued to increase. Up to two aborts were allowed in a 24 hour hour sampling routine before the full routine (either 15 or 16 samples) was undertaken on the third triggered event. This provided a capability for a very low sampling threshold (small water-level rise) but reduced the risk of false or unwanted samples being taken

A field wash routine was included in the pre-set EPIC wastewater sampler programme. This routine drew water from the sampling point, via the inlet tube, and delivered it to the sampler internal collector vessel, prior to discharge to waste, through a silicon manifold and distributor arm to a dedicated waste tube. This routine occurred immediately prior to any sample being taken by the EPIC wastewater sampler. This approach effectively purged the system, by introducing sample water into the system before the 'real' sample was required and washing all parts that might be contaminated with water from the previous sample taken.

Once the sampler programme was initiated, each 'real' sample was delivered from the internal collector vessel (purged prior to each sample) via a rotor arm to a discrete silicone tube, and then direct to the sampler bottle. The operation of the EPIC wastewater sampler (1101T) in this mode is described by Harris et al (1991) in support of pesticide loss studies

Labelling/transfer of water samples

Water samples were labelled according to Ciba Agriculture Protocol (dated November 1992). Where samples were collected from the field during the early part of the day, they were individually labelled and collected the same day by TNT for overnight transport and deliver the next day. However, on occasions this was not possible, as samples were collected too late for this method of transport. In these situations, the same labelling procedure was followed, but the 1000ml samples were split into two separate more or less equal proportions, for storage in the new Amber soda-glass bottles as used in the study. The field sample bottles were inverted three times prior to splitting to mix the contents by pouring one half of the liquid direct to the second bottle. The bottles were then labelled with the addition of an identifier of 'a' or 'b' and then frozen at -18°C until collected for overnight TNT

transport. To minimise the risk of cross-contamination the 'control' samples from 011/8/A (Moorfield) were always split and labelled for freezing, before samples from the other sites (011/8/B-D) were handled.

APPENDIX 4 - Additional ADAS GFP procedures

Good Field Practice procedures

The field studies and laboratory support procedures were fully carried out according to Good Field Practice (GFP) procedures utilising the range of ADAS Standard Operating Procedures In addition, a number of specific, separate protocols were adopted to further improve the quality of the data These were supported by GFP form procedures

ADAS Standard Operating Procedures in support of CSTR 011/8

SOP No's	Headings
Drain/	
001	Installation of SWRC weir recording systems for drain flow monitoring
003	Design and installation of weir plates for monitoring flow in open channels
004	Installation of Mini Weir Drainflow recording systems for drain flow monitoring
016/Draft	Calibration of Capacitive Probes
018	Installation of Epic Automatic Liquid Samplers for water quality sampling
019	Programming of Epic Automatic Liquid Samplers
020	Sample collection and battery change for Epic Automatic Liquid Sampler
021	Manual sampling for water quality analysis
024/Draft	Installation and use of Capacitive Probes for water level monitoring
030	Installation and maintenance of SWRC Pressure Transducer systems
034	Installation and maintenance of Tipping Bucket Rain Gauge
035/Draft	Installation and use of small Wind Generators
Datel/	
005/Draft	Installation of Campbell
026/Draft	Programming of Campbell dataloggers
028/Draft	Data capture and transfer from Campbell dataloggers via telemetry link
036/Draft	Installation and use of radio telemetry equipment

Field access

All personnel visiting the trial site completed an access form. This form enabled the areas visited to be monitored and the precautions taken to minimise the risk of contamination of the water courses to be documented. This process was supported by a strict requirement that no vehicle entering the Foxbridge and Longlands fields left the site by the metalled farm access track that ran through the Moorfield catchment. The tractor used to apply the test chemical returned to the farm utilising an old roadway to the south of the study area.

Manifold washing routines

To minimise risk of contamination of water samples taken by the EPIC wastewater samples several additional measures were introduced. In particular, the basic water sampling and purge routine was supported by a comprehensive washing procedure of the silicon manifold assembly between each activated sampling programme. The washing routine was undertaken in an area of a laboratory dedicated to the study. All wash routines were undertaken by distilled water, prepared from a 'Loughborough' pattern still, used only in support of this study. The description of the Protocol undertaken to GFP requirements is given below. This protocol includes the methodology also adopted in the field during each change of the manifold assembly to further reduce the risk of contamination of the sample bottles by the field operator. New 1000ml Amber soda-glass bottles, supplied by Lewis & Towers, were used throughout this study. Each bottle was transported to the sampler installation, as delivered by the manufacturer with dust-cap in situ. Co-Polymer caps and seals with a PTFE inner disc were added after collection of samples. Any bottle that had not been used as part of a triggered sampling procedure was discarded during the field manifold assembly change and a new bottle inserted in its place.

INSTRUCTIONS FOR REMOVING SAMPLES FROM EPIC AND SETTING UP FOR NEXT SAMPLING EVENT AT EACH SITE

Equipment List

For each Epic sampler (5 in total):

1. Plastic crate containing 23 1000ml amber glass bottles (arranged as in Fig 1). Bottle dust caps must all be in place and undamaged.
2. 23 numbered tags for above.
3. Epic manifold with correct identification number for site - pre washed and carried as described in the washing protocol.
4. 23 bottle caps with Teflon inserts.
5. 2 clean pairs of surgical gloves.

Plus

1. Epic programmer.
2. Key to CIBA padlocks.
3. Bag to carry soiled gloves, bags and dust caps.

NOTE - There are 2 EPIC samplers at site 011/8/B (Upper drain site 5 MAFF+IH). The one furthest from the fence is marked alpha and is the primary sampler. The other is marked beta and is the back up sampler. This procedure should be followed for both samplers, although samples from the back up sampler will normally be discarded after consulting SWRC.

INSTRUCTIONS FOR REMOVING SAMPLES FROM EPIC AND SETTING UP FOR NEXT SAMPLING EVENT AT EACH SITE

Procedure

A) Logger suspend switch

Before emptying the samplers the logger suspend switch must be operated at the logger box for each site. For site 011/8/A (ADAS Morfield) the logger box (grey plastic) is mounted on the platform nearest the weir.

For sites 011/8/B (Upper drain site 5 MAFF + IH), 011/8/C (Upper gauging site 1 MAFF) and 011/8/D (Drain site 3 MAFF) the logger boxes (grey plastic, marked with the site code) are located inside the small shed at 011/8/B (Upper drain site 5 MAFF + IH).

In all cases turn the plastic "key" and open the hinged box front.

The logger suspend switch is mounted on a small grey plastic box and is marked "suspend" and "normal". There is a red LED adjacent to the switch.

Move the switch to the "suspend" position and check that the red LED lights.

THE SWITCH MUST BE RETURNED TO THE "NORMAL" POSITION AFTER SAMPLE COLLECTION / RESETTING THE EPICS.

INSTRUCTIONS FOR REMOVING SAMPLES FROM EPIC AND SETTING UP FOR NEXT SAMPLING EVENT AT EACH SITE

B) Collecting samples

1. Epic sampler

1.1 At the wooden Epic box unlock the padlock and open up the front and lid of the box to give access to the Epic sampler and sample bottles.

1.2 Push back the metal handle on top of the Epic and open the hinged lid.

1.3 Remove the black rubber shroud from the programmer plug and carefully fit the programmer unit.

The display should now be as Fig 2 - with "RUN PROGRAM" flashing.

If this is not the case contact SWRC for advice/to report the fault.

TEL. 0223 840011 Try Tim Pepper, Adrian Muscutt or Steve Rose

1.4 Assuming all is well press button (1) on the programmer unit (Fig 2) and "RUN PROGRAM" will stop flashing.

1.5 Close the Epic lid and bring the metal handle back to vertical.

1.6 Disconnect the input hose from the Epic by pulling the flexible hose off the metal input tube.

INSTRUCTIONS FOR REMOVING SAMPLES FROM EPIC AND SETTING UP FOR NEXT SAMPLING EVENT AT EACH SITE

1.7 Lift the Epic off its base and place on a clean surface - eg top of a wooden Epic box.

2. Remove sample bottles

2.1 Check that all bottles have numbered tags and the layout corresponds to Fig 1.

2.2 Don a clean pair of disposable surgical gloves and remove sample tubes from all 23 bottles - checking that each tube was located in a similarly numbered bottle. - ie tube 1 to bottle 1 etc.

2.3 Remove crate containing bottles from Epic box and place on a clean surface.

2.4 Install sealing caps with teflon inserts on all bottles.

2.5 Label each bottle in accordance with FORM CIBA CSTR 011/8 SAMPLING PROTOCOL AFTER APPLICATION OF TEST CHEMICAL (N), (A1), (A2) or (S).

2.6 If number of filled sample bottles not as expected, or if any bottles are only partially full contact SWRC.

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NOTE - Once bottles have been used (IE the dust caps have been discarded), any spare bottles whether they contain water or are empty should be discarded during bottle changes to avoid any risk of contamination. This will apply for example to bottles 17-23 which will need to be discarded on a NORMAL sampling (bottles 1-16 sampled) or on a A1 or A2 manifold change procedure.

INSTRUCTIONS FOR REMOVING SAMPLES FROM EPIC AND SETTING UP FOR NEXT SAMPLING EVENT AT EACH SITE

3. Remove manifold

3.1 Disconnect the wash waste tube from the manifold (marked "W") at the join between the rigid and flexible hoses.

3.2 Remove the 3 pins securing the manifold to the Epic base.

3.3 Lift away the manifold assembly and place in a clean plastic bag for return to cleaning point.

4. Install new set of sample bottles

4.1 Fit numbered (1 to 23) tags to the neck of the new bottles corresponding to the layout in fig 1.

4.2 Slide the crate containing bottles into the Epic box. Bottle number 1 should be front left (Fig 1). Ensure that the dust caps are still attached to the bottles.

5. Install new manifold

5.1 Don a new, clean pair of disposable surgical gloves.

5.2 Partially remove the fresh manifold from its plastic bag, leaving the sample delivery tubing protected.

INSTRUCTIONS FOR REMOVING SAMPLES FROM EPIC AND SETTING UP FOR NEXT SAMPLING EVENT AT EACH SITE

5.3 Install the manifold tray in the Epic base and locate the 3 pins in the corresponding holes in the manifold and base.

5.4 Starting with tube number 1 remove the sample delivery tubes from the protective plastic bag and install in the corresponding bottle, having first removed the bottle dust cap.

5.6 Refit the wash waste tube.

5.7 Take away the dust caps, soiled plastic bag and gloves for disposal.

6. Replace Epic

6.1 Relocate Epic on its base - the "lug" on the wall of the Epic locates in a cut-out on the wall of the base.

6.2 Reconnect the input hose to the metal input pipe of the Epic

6.3 Push down the metal handle and open the lid of the Epic.

6.4 Push button 4 on the programmer unit (Fig 2).

"RUN PROGRAM" (Fig 2) will now start flashing and you will hear the distributor arm move round to its start position.

If this is not the case contact SWRC for advice/to report the fault.

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INSTRUCTIONS FOR REMOVING SAMPLES FROM EPIC AND SETTING UP FOR NEXT SAMPLING EVENT AT EACH SITE

6.5 Remove the programmer unit and replace the protective rubber shroud.

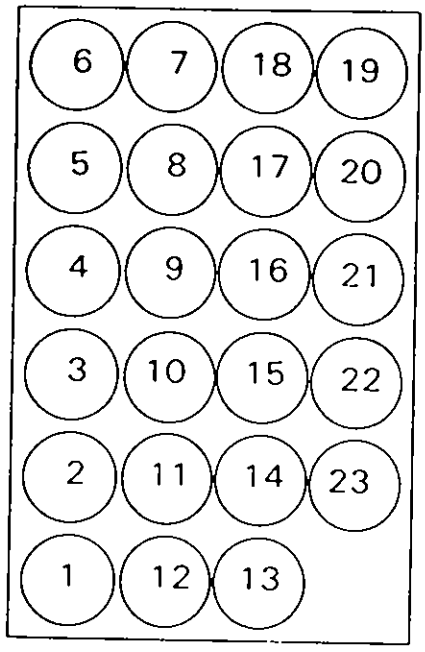
6.6 Close the Epic lid and move the metal handle to the vertical.

6.7 Close up the wooden box and lock the padlock.

AT THE LOGGER BOX MOVE THE SAMPLE SUSPEND SWITCH TO "NORMAL"- RED LED OUT

FIG 1 - Location of bottles within crates

A) 011/8/D (DRAIN SITE 3 MAFF)



B) All other sites

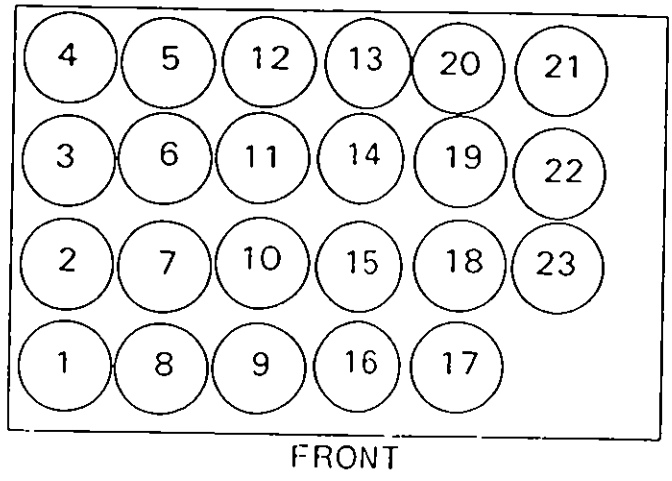
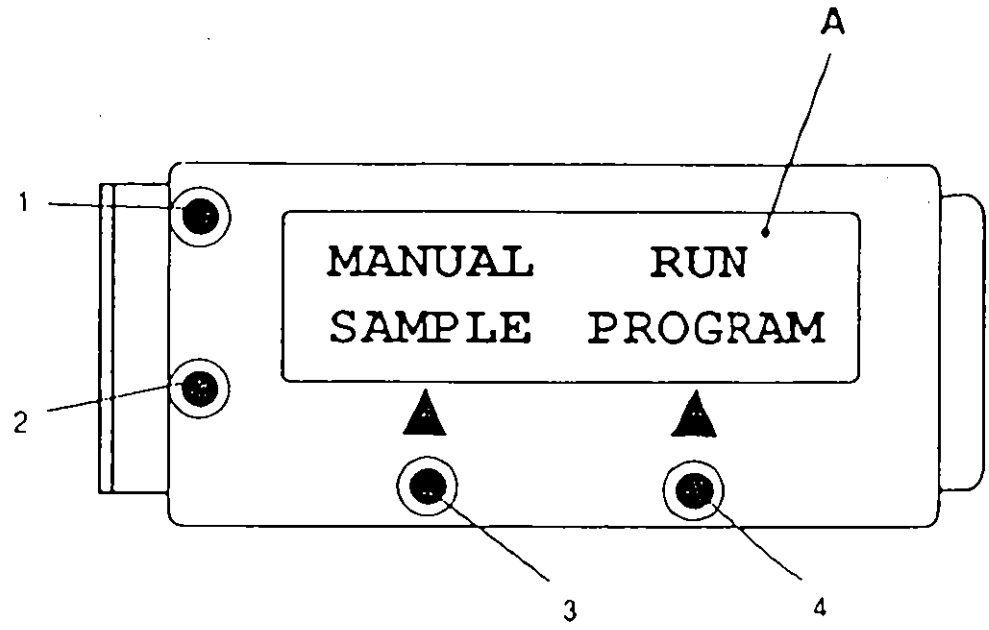


FIG 2 - Epic programmer unit



A Display - "RUN PROGRAM" flashing when operational

Pushbuttons

1 Reset

2 Program

3 • 4 Set or select option

MANIFOLD ASSEMBLY WASHING PROCEDURE - Automatic water samplers

Requirement for cleaning

As part of the sampling programme it is necessary to completely replace and wash the manifold assembly every time any bottles are replaced. This procedure is necessary because although the EPIC sampler includes a wash routine (to waste), the manifold tubes leading to the individual bottles are not pre-washed and a risk of contamination (from earlier samplings) remains.

THIS ROUTINE APPLIES EVEN IF ONLY FOUR BOTTLES (A1) ARE BEING REPLACED AS THE SAMPLING PROGRAMME WILL RESET TO ZERO (THUS RE-USING THE FIRST FOUR SAMPLING TUBES).

Definition

A complete manifold assembly consists of the moulded, 24 channel, funnel/tray in uncoloured polyethylene, supplied by Epic, with a delivery tube attached to each channel except channel 0 (the "wash" channel). Each delivery tube is constructed, in three parts, from different diameters of surgical grade silicone rubber tubing bonded with acetoxysilane adhesive. The top part is a diameter reducer which is a push fit onto one of the channel outlets on the funnel/tray. The bottom part is a push fit plug and air-bleed tube, to fit the sample bottle. The centre section is a transport tube individually cut to the correct length to bridge between funnel tray and sample bottle for that channel. The three parts are joined by push-fit inserts of PTFE tubing.

Channel 0 of the funnel/tray is fitted with the top part only of the delivery tube, for connection to a waste water drain tube. Each manifold is marked indelibly with a unique identification number referring to the sampling station for which it is to be used. There are five manifold assembly sets in the Ciba Agriculture experiment (two EPIC samplers at 011/8/B - Upper drain site 5 - MAFF + IH). Each delivery tube is indelibly marked with the channel number it carries on that manifold (1-23). Two sets of manifolds are provided for each location, one for immediate use and one as a spare. This should give approximately 24 hours or more for the wash routine to be carried on each manifold when removed from the field.

Cleaning procedure

1) Each time a set, or part - set of sample bottles is changed, a freshly cleaned manifold must be fitted to convey the next set of samples from the automatic sampling equipment to the sample bottles.

2) Clean manifolds must be carried from the cleaning point (laboratory) to the field sampling station inside a sealed, new, clean bag made of food grade polyethylene, at least 250 gauge in thickness (provided by SWRC). These bags will be provided for this purpose only, stored in a clean, closed container and used once each only. They should be discarded immediately after use to avoid any risk of subsequent inadvertent use (and contamination).

3) After capping and removing sample bottles, the field operative will remove the previous manifold from the sampling installation, and immediately place it in a clean black polythene (dustbin) bag for return to the cleaning point. A polyethylene bag previously used for the transport of a clean manifold assembly will not be acceptable. (The bag used to enclose the manifold removed, for return to the cleaning point and storage until washed, will then be discarded.)

4) The operative will then carefully don a new, clean pair of disposable surgical gloves in order to remove the fresh manifold from its bag and fit it to the sampler and the new set of sample bottles. (Any gloves worn to handle the previous samples will first be carefully removed and disposed of remote from the fresh manifold.) Before opening the bag containing the manifold, check that it is the correct one for the sampling station to which it is to be fitted. Care must be taken to avoid contact or other contamination of those surfaces of the manifold assembly which will come into contact with the water samples. Initially the polythene bag should be removed only partially from the manifold assembly, far enough to expose the 24 - way funnel/tray and allow its fitment to its support but continuing to enclose and protect the bottom ends of the delivery tubes. The bag will be left thus in place until the delivery tubes are removed from it, one by one, for immediate fitment to the new sample bottles.

5) The cleaning point (laboratory) will be set up in a clean room remote from the handling of agrochemicals and any soil or crop samples, equipment, etc. which might be contaminated with the chemical under investigation.

6) The cleaning point will be furnished with equipment to provide distilled water to a purity level acceptable for routine apparatus washing in an analytical chemistry laboratory. (The still will be provided by SWRC for this purpose). Distilled water will be produced as required from local mains drinking water, the first litre of each production run being discarded, and the distilled water then run directly into the "WASH" vessels (eight to provided by SWRC) which will remain lidded to exclude airborne contaminants.

Distilled water will also be run into "SPARE" vessels (see below), and stored with the lids in place to avoid airborne contaminants.

7) The washing vessels are bins of approximately 25 litres capacity, formed from food grade uncoloured polyethylene, with close fitting lids of the same material, furnished with sealable filler tubes of surgical grade silicone rubber and PTFE, for connection to the distilled water generator, and with filtered (0.45 micron) vent tubes. Each vessel (five to be used for the "WASH" routine) is capable of holding a complete manifold plus delivery tube assembly such that all the silicone rubber components are totally immersed in at least 20 litres of distilled water. The vessels and their lids should be thoroughly washed with distilled water before and after use. If at any time during their use there is any evidence of sediments or biological growths developing within the vessels, they should be cleaned out with tap water and clean brushes only, and thoroughly rinsed with fresh distilled water before further use.

8) On return from the field, each manifold assembly will be examined for damaged or lost components, and any visible deposits. Any necessary repairs will be immediately notified to SWRC for advice and repair.

Tel: 0223 840011 Try Andy Thorburn, Tim Pepper or Steve Rose

Deposits should be removed by scraping/brushing as necessary and by thorough washing with clean mains tap water. The assembly should then be held aloft to drain until dripping has effectively stopped. It should then be placed in a "WASH" vessel which will have been previously filled with distilled water; each "WASH" vessel will be labelled for the manifold sampling location (ie. each of the five "WASH" tanks will service its own site location).

The manifold should remain with the silicone rubber components totally immersed in distilled water for at least 30 minutes and agitated vigorously at least once to dislodge any particulate contamination still present on the inner or outer surfaces.

9) After the washing period (at least 30 minutes) is complete, the manifold assembly should be lifted from the tank by an operative wearing a new pair of clean, disposable surgical gloves and held aloft, briefly, to drain. Then approximately 50ml of distilled water from the "STORE" vessel (not the "WASH" vessel) should be poured through each channel, using a clean glass beaker kept for this purpose only, to purge any water retained from the rinse stage. After holding aloft for further draining (shake), the manifold assembly should then be lowered carefully into a new, clean, undamaged polyethylene bag which should be sealed and used for storage and transport to the field (See [2 and note below]).

10) Usually a batch of five manifolds will be returned for cleaning. When all five manifold assemblies have been fully washed and each put into their polythene bags, the distilled water in the "WASH" bins should be discarded and each "WASH" bin and lid thoroughly swilled with clean distilled water from the three "STORE" bins. The clean distilled water should be replaced in the three "STORE" vessels and the five "WASH" vessels from the still, as soon as possible, so as to be ready for the next washing cycle.

11) All vessels will be kept lidded at all times except as necessary for the introduction and removal of manifolds and the transfer of water.

12) A record will be kept of each occasion in which a wash cycle is performed including when each vessel is filled and rinsed. This is essential as a wash cycle may be performed at one location only following an A1/A2 abort sampling programme.

Note:

Location 011/8/B - Upper drain site 5 (MAFF + IH) has two sampling EPICS (individually labelled). The "WASH" vessels must be clearly marked to avoid cross contamination during washing.

To seal bags, roll top of bag over and seal with staples or tape to prevent any risk of mud/dust entering the bag during transport.