THE DRINKING WATER INSPECTORATE

SUMMARY REPORT ON THE 2005 & 2006 PESTICIDE AUDIT TRAILS

THE DRINKING WATER INSPECTORATE - PESTICIDE AUDIT TRAILS FOR 2005/06 CARRIED OUT BY MR STEVE SCOTT

Overall Summary and Conclusions

1 Introduction

1.1 During 2005 and 2006 Mr Steve Scott, Temporary Inspector, undertook the annual pesticide vertical audits of 16 water companies in England and Wales. The other non-microbiological vertical audits of all 26 water companies were audited by Dr. Peter Whittle. A risk based approach was taken on the number of samples to be audited, based on the relative size of the company in terms of population supplied and findings from previous audits.

1.2 A total of 22 samples and 11 different pesticides were audited. This compares to 59 pesticide samples audited (56 isoproturon, 3 chlortoluron) in 2004. In terms of samples per parameter per company, this amounted to:

Bentazone	2 companies; 2 samples
Carbendazim	5 companies; 5 samples
Carbetamide	4 companies; 4 samples
Fluroxypyr	1 company; 1 sample
Glyphosate	1 company; 1 sample
Heptachlor epoxide	2 companies; 3 samples
MCPA	1 company; 1 sample
MCPP (Mecoprop)	1 company; 1 sample
Permethrin	2 companies; 2 samples
Prometryn	1 company; 1 sample
Trietazine	1 company; 1 sample

All of the samples selected for audit were taken during 2005, the earliest being 5th January and the latest 13th June. 3 companies were audited for 3 samples, 2 companies were audited for 2 samples, while the remaining 11 companies had 1 sample audited.

1.3 Individual reports were produced for each company. Mr Scott made a total of **16 recommendations** on matters, which in his opinion, could result in a foreseeable risk of breaching a regulatory duty. Mr Scott also made 17 suggestions on matters of good practice.

1.4 Mr Scott would have recommended **enforcement action** to the DWI, in one instance, for deficiencies in AQC methodology, had this not already been initiated by Dr Whittle following a joint visit to the laboratory.

1.5 Some of the recommendations and suggestions were specific to the individual company, but there were a number of recurrent deficiencies. This report

summarises Mr Scott's main findings and includes a short review of the various analytical methods and their method performance. Mr Scott found record keeping and the provision of information to be generally very good.

1.6 Mr Scott did not visit all the laboratories undertaking potable water analysis on behalf of statutory water companies in England and Wales, as part of the audit process. The few analytical queries that arose from the audits were resolved by post, e-mail or phone calls. Mr Scott would like to thank the laboratory staff and water quality representatives for their help and timely responses to all enquiries.

2 Overall Conclusions

2.1 Mr Scott concluded that:

- The presentation of the audit data was generally excellent. The majority of companies had made considerable efforts to ensure the data was presented in a fashion that aided the audit, which was greatly appreciated by Mr Scott. However a number of companies did not follow fully the request for information, especially in terms of submitting a full record of an analytical run. The common areas for missing data were system suitability data, calibration curves, raw data, chromatograms and result calculations.

- Only 2 of the 16 companies showed problems with sample scheduling and regularity of sampling.

- In general the standard of analysis was very good. The use of LC-MS continues to increase in popularity with its associated ease of use and improved confidence of results.

- The use of surrogate and internal standards is to be commended and their use encouraged for those methodologies currently not utilising them. A consequence of monitoring these standards will indicate the suitability of the technique when used to analyse a variety of water types. This is especially important for contract laboratories where it may analyse a wide range of waters.

- The calibration procedure is an essential step in the analytical procedure. It is somewhat alarming then, that several audits indicated that laboratories had removed one or more points from a calibration curve without adequate explanation. The consequence of this action is that it leaves a huge uncertainty with regards to the validity of the results being quoted for routine samples with unknown concentrations.

- The AQC was generally satisfactory although those for Heptachlor epoxide, where the PCV had been reduced from 100 to 30 µg/l, had not been updated to reflect the regulatory change.

- Reporting was largely satisfactory, although there was an issue relating to the reported limit of detection (LOD). Reported LODs were not being calculated from the validation data in accordance to DWI information letter 18/99.

3 Issues that resulted in recommendations and suggestions to the industry

3.1 Regularity of scheduling and sampling

Mr Scott adopted the same approach to defining regularity as Dr Whittle, i.e. +/- 25% of the target date. On that basis two consecutive samples should not be taken closer than half the sampling interval or apart by one and a half times that interval, where the interval was 365 divided by the number of samples scheduled for the year. One company finished its schedule too early with the result that the end of the year was not sampled. Another had organised the schedule so that the laboratory had minimal workload over the summer holiday period with a subsequent failure in regularity requirements.

3.2 Sampling in general

In general the samplers' records were good but there were several cases where the reasons for using alternative sampling points or dates were not recorded. Mr Scott would suggest that the samplers' records be annotated at the time of sampling with the reason.

3.3 Time between sampling and analysis

Mr Scott found storage records and times good. Although not all companies had completed stability trials, the times between sampling and start of analysis were within generally accepted limits. Indeed the majority of audits the analysis started within three days of sampling.

3.4 Method performance

A wide range of techniques were used to extract and analyse the 11 different pesticides. A summary of the performances is provided in a table at the end of this report.

3.4.1 The majority of the analyses audited used a surrogate standard (SS) which is normally a compound(s), usually an isotopically labelled analogue, that is added to the sample immediately prior to the start of the analysis. The purpose of this compound(s) is to monitor the performance of the technique. It may also be used to correct the reported concentration by adjusting the value for recovery variations. Several of the methods did not incorporate a SS. Mr Scott was concerned that for these methods, there was no means to check that the sample was extracted or analysed correctly. Mr Scott also had issue with one company that adjusted the reported limit of detection in line with the recovery of these SSs. It was observed that within one run the SS had a recovery range

from 0 to 340%. In this case it would indicate that the method was not suitable for the samples being analysed.

3.4.2 Mr Scott observed that many of the procedures lacked a detailed section explaining the calibration calculation and its associated acceptance criteria. Indeed, in 3 of the 22 audits the laboratories had removed one or more points from a calibration curve without adequate explanation. The implicit inference is that these points did not fit the curve. The difficulty with this argument is that although this may have some support for known solutions, the consequence is that it leaves a huge uncertainty with regards to routine samples with unknown concentrations. This is particularly worrying when these same samples also utilise a SS to correct for minor recovery issues which should improve curve fitting routines.

3.4.3 Mr Scott was concerned that five years after the issuing of the DWI information letter 18/99, four companies had still to adopt the guidance. These companies were reporting incorrect LODs, e.g. validation data produced a calculated LOD of 0.00244 µg/l which is reported as <0.01 µg/l (should be <0.003 µg/l). Also, the issue identified in 3.4.1 regarding the recovery of SSs was used to change the LOD from <0.003 µg/l to <0.018 µg/l for a sample.

3.4.4 The larger companies often use several instruments to analyse the same suite of pesticides. It is important that in these situations, that each instrument has its own supporting data to demonstrate its suitability. Mr Scott was not always provided with this information and, although it is essential that the data are annotated to reflect which instrument has been used to analyse the sample, this did not occur.

3.5 Analytical Quality Control

Mr Scott noted that apart from one company, as reported in Dr Whittle's summary, that the AQC data were good.

3.5.1 The change in the PCV for Heptachlor epoxide from 0.1 µg/l to 0.03 µg/l should have been reflected in a corresponding change in the nominal AQC value. This had not occurred in two companies.

3.5.2 While reviewing the investigations associated with quality control failures or AQC chart reviews Mr Scott was concerned that in the majority of cases these investigations were minimal. Often, the only action reported was the remaking of standards without supporting documentation. Mr Scott would endorse Dr Whittle's view that "*the effort involved in undertaking and documenting thoroughly any investigations and correctly setting AQC limits would be repaid through fewer failures, less re-work and re-sampling"*.

3.5.3 If multiple instruments are being used for analysis of a pesticide, then each instrument should have its own AQC chart as opposed to combining them on a single chart. A3.11 of the *Guidance on the Water Supply (Water Quality)*

Regulations 2000 (England) May 2005, states that '*if the internal AQC record subsequently shows a significant difference in performance between methods each system should then be fully validated*'.

3.6 Proficiency testing (PT)

3.6.1 Although the majority of the methods audited had been evaluated using external proficiency testing, Mr Scott was concerned that two-thirds of the audits were not subject to PT using the pesticide being audited. It is understandable that where a method is analysing a large suite of compounds that it may not be possible to PT every compound; those compounds that are tested should reflect, as near as possible, the physical and chemical characteristics of all compounds within the suite. Mr Scott was of the opinion that the diversity of the compounds within a suite meant that this was not always the case and he made 9 suggestions, where this occurred, that they approach their PT organisation and request the compound is included in future schemes. Mr Scott observed that the quality, recording and any subsequent investigation of the PT that was done, were very good.

3.6.2 Glyphosate was one compound that will require further investigation. Currently there are only two participants in the PT scheme. The results from the last round indicated that both laboratories had a negative bias but because of the limited data set and the uncertainty that ensues from such a situation then it was decided that the PT flags would be removed for this round. Mr Scott's review of one company's glyphosate AQC data showed that there were long term bias issues that had not been fully investigated. It is worrisome that there are only two laboratories measuring the majority of the water companies' glyphosate concentrations in water and that there is an inadequate external audit of the methodology.

4 Specific recommendations to DWI

Mr Scott recommends to DWI that:

- Consideration should be given to issuing guidance on incorporating surrogate and internal standards to all methods used to monitor organic determinands.
- Consideration should be given to amending the '*List of items required for a full audit trail*' to include a request for the calibration, AQC and PT data for all compounds that are analysed within an analytical run. There should also be a request for the validation data of all 'identical' instruments when one more than one instrument is used to analyse a parameter.
- Consideration should be given to issuing a reminder to companies to follow the guidance on reporting LODs given in DWI Information Letter 18/99.

- Consideration should be given to issuing guidance on the use of AQC data for methods that use identical instruments to measure a parameter.
- The analysis of Glyphosate is worthy of further attention in the future, with particular emphasis on the PT and the suitability of the method to analyse the compound in a variety of water matrices.

Summary of method performance

Parameter	Calibration Range µg/l	LOD µg/l	AQC Nominal µg/l	Precision %	Trueness %	Method	Maximum Storage Time (Days)
Bentazone	0 – 0.200	0.0026	0.1	7.7	102.3	SPE, derivitisation, GC-MS	51
Bentazone	0 – 0.200	0.0027	0.09	-	-	SPE, LC-MS/MS	14
Carbendazim	0 – 0.300	0.002	0.1	10.4	96	SPE, LC-MS (+ UV confirmation)	10
Carbendazim	0 – 0.150	0.0085	0.1	18.5	102.2	SPE, LC-UV (254 nm)	ASAP
Carbendazim	0 – 0.300	0.004	0.1	-	90.7	SPE, LC-UV-DAD	7
Carbendazim	0 – 0.500	0.0038	0.1	18.2	94.3	DAI, LC-MS	14
Carbendazim	0 – 0.125	0.0069	0.1	-	96.6	SPE, LC-MS	-
Carbetamide	0 – 0.400	0.0036	0.1	5.2	99.6	SPE, LC-UV-DAD	21
Carbetamide	0.03 – 0.300	0.0051	0.1	4.7	101.6	SPE, LC-UV-DAD	14
Carbetamide	0 – 0.400	0.005	0.1	13.6	98.8	SPE, LC-MS	55
Carbetamide	0 – 0.400	0.0047	0.09	-	-	SPE, LC-MS	ASAP
Fluroxypyr	0 – 0.200	0.0036	0.1	4.5	101	SPE, derivitisation, GC-MS	51
Glyphosate	0.02 – 0.300	0.0062	0.1	30.8	93.6	SPE, LC-derivitisation-fluorescence	14
Heptachlor epoxide	0 – 0.120	0.0015	0.03	11.4	98.7	Iso octane extn., GC-MS	1 month
Heptachlor epoxide	0 – 0.150	0.004	0.03	-	-	SPE, GC-MS	14
MCPA	0 – 0.500	0.003	0.1	8.9	95.7	SPE, LC-MS	14
MCPP (Mecoprop)	0 – 0.500	0.004	0.1	5.8	82.8	SPE, LC-MS	14
Permethrin	0 – 0.100	0.010	0.06	-	-	Hexane extn., GC-ECD	14
Permethrin	0 – 0.240	0.001	0.1	14.8/13.5	100/102	Iso octane extn., GC-MS	1 month
Prometryn	0 – 0.200	0.008	0.1	-	-	SPE, LC-MS	-
Trietazine	0 – 1.00	0.003	0.1	5.5	95.7	SPE, LC-UV	14