Chapter Five

Analysis of Target Analytes in Selected River Waters Sourced in South Wales
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5.1 Aim

The aim of this research is to apply the sample preparation and analysis procedures discussed in previous chapters to recover and detect the target analytes (listed in Table 1.2) in samples of river water.

Several rivers that run through South Wales were studied namely the Rivers Wye, Ely, Ogmore and Taff. These were chosen as examples of rivers passing through agricultural, industrial and semi-rural areas. Each river rises in the mountains of South and Mid Wales and flows into the Severn Estuary.

Water samples were obtained from each river at specific points along their course, starting close to the river source as practicably possible and additional points downstream.

These samples were used to determine the limits of detection, limits of quantification and method detection limits using real water samples.

Finally each of the rivers were studied using the single multiresidue analysis and recovery method to deliver a snapshot of the quality of the South Wales river system in respect to the priority pesticide load.
5.2 Sampling Locations and River Descriptions

Table 5.1 shows the date and Global Positioning Satellite (GPS) co-ordinates for each river location sampling point on the River Wye, River Ogmore, River Ely and River Taff.

**Table 5.1** The GPS Co-ordinates of the river sampling points

| River | Location Name      | Date              | GPS Co-ordinates     |
|-------|--------------------|-------------------|----------------------|
| Wye   | Newbridge-on-Wye   | 08/05/09 and 15/07/09 | N 52.21360 / W 3.47083 |
|       | Llangurig          | 08/05/09          | N 52.39470 / W 3.60443 |
|       | Symonds Yat East   | 08/07/09          | N 51.84409 / W2.64210 |
|       | Kerne Bridge       | 15/07/09          | N 51.86931 / W 2.60965 |
| Ogmore| Bwlch Mountain     | 14/07/09          | N 51.64057 / W 3.55126 |
|       | New Mill           | 14/07/09          | N 51.55784 / W 3.56314 |
|       | Ogmore Castle      | 14/07/09          | N 51.48028 / W3.61216 |
| Ely   | Thomastown         | 08/05/09          | N 51.57663 / W 3.43575 |
|       | Ely Valley         | 08/05/09          | N 51.55714 / W 3.41104 |
|       | Peterston-super-Ely| 08/05/09          | N 51.47683 / W 3.32364 |
|       | St Georges         | 08/05/09          | N 51.48396 / W 3.29788 |
| Taff  | Storey Arms        | 08/05/09          | N 51.86810 / W 3.47083 |

5.2.1 River Wye

The source of the River Wye is in the Welsh mountains and it flows through the towns of Rhayader, Builth Wells and Hay-on-Wye (Figure 5.1). It passes through the town of Hereford then on to Ross-on-Wye, Symonds Yat and Tintern. For the lower 16 miles of its course it forms the border between England and Wales then enters the Severn estuary close to Chepstow. Figure 5.1 shows the sampling points of the river at Llangurig, Newbridge-on-Wye (a village south of Rhayader), Symonds Yat East and Kerne Bridge.

The Wye is popular for many leisure and tourism activities including boating, canoeing, kayaking and water rafting as there is approximately 100 miles of navigable water with
access points all along the course of the river [1]. It is also popular for salmon and trout fishing.

It is suitable as a source of drinking water; however certain rivers and streams in the upper catchment suffer from acidification and localised pollution problems from inadequate sewerage and agricultural sources [2].

The Wye has a wide variety of plant and animal life along its length. There are algae and mosses in the upper sections of the river and invertebrates, crustaceans and birds all along its length. More than thirty species of fish have been found along the Wye and many birds nest along its banks [3].

In the late 1950s, many of the mammals that lived along the banks were killed off due to use of highly toxic pesticides in the area. Many mammals have returned to the Wye, perhaps as evidence of decreasing environmental pollution but the otter still only inhabits its tributaries [3]. Figure 5.2 shows the sampling point at Symonds Yat East at the launch steps of the boating club.
Figure 5.1 Sampling points on the River Wye
5.2.2 River Ogmore

The River Ogmore runs generally from north to south from its source in the Bwlch Mountains north of the village of Nantymoel. It flows through the Ogmore Valley, an area with a traditional mining heritage, to the industrial town of Bridgend and then onwards into the Severn Estuary between the beach resort of Ogmore-by-Sea and the sand-dunes of Merthyr Mawr.

The river supports a population of variety of aquatic invertebrates and provides good spawning for the salmon, sewin and trout due to the lack of a barrage at the mouth of the river. However pollution problems do exist in the river due to the proximity of large industrial sites, abstraction for irrigation and litter [4].
Sampling of the River Ogmore took place at its source in the Bwlch Mountains, the small village of New Mill and a point close to Ogmore Castle, short distance downstream from a sewage treatment works. Figure 5.3 shows the source of the Ogmore in the Bwlch Mountains.

![Image of the source of the River Ogmore](image)

**Figure 5.3** The source of the River Ogmore

### 5.2.3 River Ely

The source of the Ely lies in the mountains to the south of Tonypandy in the county borough of Rhondda Cynon Taff. It flows through the towns of Tonyrefail, and through the valley east of Llantrisant then through Talbot Green before heading to Miskin and onto the Severn Estuary on the west of the city of Cardiff.

Prior to the 1980s it had received large volumes of poorly treated or untreated sewage from the urban areas in the South Wales Valleys. This continued until the construction of sewage treatment works at Miskin and Rhiwsaeson. The quality of the effluent continued to cause pollution until the late 1980s and large industrial sites discharged into the river. The intervention of the Environment Agency has greatly reduced river pollution in the Ely [5].
Figure 5.4 shows the sampling point at St. George on the River Ely. Sampling of the River Ely took place close to the source in Thomastown (south of Tonyrefail) then further sampling points were in the Ely Valley and the villages of Peterston-Super-Ely and St. Georges in the Vale of Glamorgan (Figure 5.5).

Figure 5.4 River sampling point on the River Ely at St Georges
Figure 5.5 Sampling points on the River Ogmore and River Ely
5.2.4 The River Taff

The River Taff rises in the Brecon Beacons National Park and flows south through industrial heartlands of central South Wales including Merthyr Tydfil, Pontypridd and out into Cardiff Bay and the Severn Estuary. Sampling of this river took place close to source in the Brecon Beacons at Storey Arms (Figure 5.6). This location was chosen as the water sampled here would be expected to be the cleanest and free of contaminants or pollutants. This water was then used for method development of the analytical method. Samples of this water were spiked with known concentration of analytes to determine sample recoveries after SPE extraction compared to High Quality (HQ) water spiked with the same analytes at the same concentration.

Figure 5.6 Source of the River Taff (Taff Fawr) in the Brecon Beacons, Storey Arms

The Taff Fechan and Taff Fawr rise in the Beacons they meet north of Merthyr Tydfil to become the River Taff. It flows uninterrupted through the countryside until it reaches the
town of Pontypridd. Here it is met by the Rhondda River and continues south to the city of Cardiff and into Cardiff Bay [6].

5.3 Sampling Procedure

All glassware used for the collection of samples including location sampling bottles were silanised prior to sampling. This is a standard laboratory technique that prevents sample loss by deactivating the glass surface. Silanisation masks the polar Si-OH groups on the glass surface by chemically binding a non adsorpative silicone layer to it. Glassware was soaked in 5% dimethyldichlorosilane (DMDCS) in toluene and then rinsed in 100% toluene and finally in 100% methanol [7].

Figure 5.7 Water collection at Symonds Yat East

River water samples were collected in either 2.5 litre or 1.0 litre silanised glass bottles and sealed with Teflon faced phenolic caps. A sampling beaker attached to a 2 metre long arm was used to collect approximately 400 cm$^3$ aliquots of water at a time (Figures 5.7 and 5.8).
The samples were collected a short distance from the river bank in faster flowing water, and in a series of smaller aliquots to give a more representative sample of water. The water samples were then returned to the laboratory, stored at 4 °C and extracted within 7 days.

A series of experiments were carried out on HQ water and river water samples to establish the analytical figures of merit for the optimised analytical procedure described in following section.
5.4 Laboratory Analyses of Samples

Four separate stages of research were performed to determine the concentrations of analytes in the Rivers Wye, Ely, Ogmore and Taff. The four stages were performed to establish the concentration losses during the SPE process and the reproducibility of results.

Investigation 1: Five day sample stability study.
Standards of all compounds of over seven concentration (10 μg l\(^{-1}\), 50 μg l\(^{-1}\), 100 μg l\(^{-1}\), 250 μg l\(^{-1}\), 500 μg l\(^{-1}\), 750 μg l\(^{-1}\) and 1000 μg l\(^{-1}\)) were added to HQ water. The same standards were analysed over a five day period to determine the peak area response and so determine sample stability over a period of time. The samples were stored in the dark refrigerated at 4 °C and between analyses.

Investigation 2: Seven day instrument interday variation study.
Standards of all compounds at a concentration of 100 μg l\(^{-1}\) were added to HQ water. Fresh standards were prepared daily for seven days and analysed to measure the peak area response and therefore determine instrument reproducibility.

Investigation 3: Investigation of analyte loss during extraction.
River water from the source of the River Ogmore taken from close to the source was spiked with the analytes under investigation. The samples were passed through filters to remove particulates and SPE to concentrate and clean up the analytes. This study was to examine the analyte losses through particulate filtration and the SPE cartridge.
Investigation 4: Determination of concentration of target analytes in river water.

The full analyses of the river water to determine the concentrations of the twelve analytes under investigation. Deuterated standards ‘set 1’ (isoproturon_d6, simazine_d10, and alachlor_d13) were added prior to filtering and SPE of the water and used to determine analyte loss due to filtration and the SPE process. Deuterated standards ‘set 2’ (atrazine_d5 and diuron_d6) were used as internal standards added to the analytes under investigation post filtration and SPE.

Table 5.2 summarises the procedures for each of the four investigation steps.
### Table 5.2  Summary of the four investigation steps

| Investigation | Description / Aim | Sample Matrix | Pre extraction conditions | SPE (Oasis MCX) | Post extraction conditions | Analysis method |
|---------------|-------------------|---------------|---------------------------|----------------|---------------------------|-----------------|
| Investigation 1 | 5 day analyte stability study (n=8) | HQ Water | _______ | No | 17 Reference standards (added at 10, 50, 100, 250, 500, 750, 1000 μg l⁻¹) | mei128 |
| Investigation 2 | 7 day instrument reproducibility study (n=8) | HQ Water | _______ | No | 17 Reference standards (added at 100 μg l⁻¹) | mei128 |
| Investigation 3 | Study to investigate analyte losses due to particulate filtering and SPE | HQ water River Ogmore (Bwlch Mountain) | 17 Reference standards (added at 10, 50, 100, 250, 500, 750, 1000 μg l⁻¹) | Yes | 17 Reference standards (added at 10, 50, 100, 250, 500, 750, 1000 μg l⁻¹) | mei128 |
| Investigation 4 | To determine concentration of 12 target analytes in river water | River Wye River Ogmore River Ely | Addition of deuterated standards (Set 1) | Yes | Addition of deuterated standards (Set 2) | mei128 |
5.4.1 The MassLynx Software

The MassLynx operating software uses the Quanlynx application manager to report the data. The software was used to present peak area response data for each injection run. The data produced was transferred to Microsoft Excel for analysis. Figure 5.9 shows an example of a typical screenshot that is produced, the sample is an atrazine compound at a concentration of 10 μg l⁻¹.

![Figure 5.9 An example screenshot of the QuanLynx software reporting the data](image)

The bottom left of the screen (Chromatogram) shows the first and second transition ion peaks for the first of eight repeat injections. The bottom right of the screen (Calibration) shows the peak area Response for each of the eight atrazine analyte repeat injections. The Residuals in this screen shows the percentage difference each point is away from the mean of the peak area response of all eight measurements.
The top half of the screen reports the results in a tabular form of file name, file type, sample concentration, retention time and first transition peak area. This data can be copied and transferred to other data analysis software. Table 5.3 shows how a copy of the information from Figure 5.9 MassLynx, QuanLynx is displayed in Microsoft Excel. This shows the results of eight repeat injections of a single sample of atrazine on a single day.

**Table 5.3** Example of the MassLynx reporting of eight repeat measurements for 10 μg/l concentration of atrazine on a single day

| Compound 1: ATRAZINE                | Name          | Type     | Std. Conc | RT   | Peak Area | ug/l  | %Dev | RRF   |
|-------------------------------------|---------------|----------|-----------|------|-----------|-------|------|-------|
| 1                                   | 24_03_09_10ugL_day02_01 | Standard | 10        | 4.28 | 2491.2    | 9.3   | -6.8 | 2.696 |
| 2                                   | 24_03_09_10ugL_day02_02 | Standard | 10        | 4.28 | 2772.2    | 10.4  | 3.8  | 2.696 |
| 3                                   | 24_03_09_10ugL_day02_03 | Standard | 10        | 4.26 | 2677.8    | 10.0  | 0.2  | 2.696 |
| 4                                   | 24_03_09_10ugL_day02_04 | Standard | 10        | 4.26 | 2569.6    | 9.6   | -3.8 | 2.696 |
| 5                                   | 24_03_09_10ugL_day02_05 | Standard | 10        | 4.26 | 2613.6    | 9.8   | -2.2 | 2.696 |
| 6                                   | 24_03_09_10ugL_day02_06 | Standard | 10        | 4.26 | 3003.7    | 11.2  | 12.4 | 2.696 |
| 7                                   | 24_03_09_10ugL_day02_07 | Standard | 10        | 4.26 | 2682.6    | 10.0  | 0.4  | 2.696 |
| 8                                   | 24_03_09_10ugL_day02_08 | Standard | 10        | 4.26 | 2715.0    | 10.2  | 1.6  | 2.696 |

Table 5.3 shows the compound name and the data for each of the eight injections. It shows the MassLynx raw data file name under the heading ‘Name’, the standard concentration under Std. Conc. the peak retention time under ‘RT’, the peak area response under ‘Peak Area’, the sample concentration under ‘ug/l’ and the percentage relative response factor under ‘RRF %Rel SD.

The automated values delivered by the software under the ‘ug/l’ column are not considered in this study as they don’t take into account the values of the deuterated standards. The concentration values are calculated through other data analysis means.
The Masslynx data was transferred to Microsoft Excel spreadsheets for data manipulation to generate graphs and tables. All the data is available electronically and where data is referred to in the text, the folder/file name and Excel Tab sheet number is given.

### 5.4.2 Limits of Detection, Limits of Quantification

The limits of detection (LOD) is the concentration of an analyte required to give a signal response equal to the background blank and three times the standard deviation of the blank whilst the limits of quantification (LOQ) are taken as ten times the standard deviation of the blank.

The MassLynx software does not detect the LOD and LOQ automatically but for a given peak the software reports signal/noise values and therefore the LOD and LOQ have been calculated manually using the following approach:

\[ \text{LOD} = 3 \times \text{RMS}_{\text{noise}} \quad \text{and} \quad \text{LOQ} = 10 \times \text{RMS}_{\text{noise}} \]

where:

\[
\text{Root Mean Squared}_{\text{noise}} = \frac{\text{sample peak area}}{\text{signal to noise}}
\]

(Equation 5.1)

For a sample of known concentration \((x)\) the calculated LOD concentration is given by:

\[
\text{concentration} = \frac{\text{LOD}}{\text{peak area}/x}
\]

(Equation 5.2)

And for a sample of known concentration \((x)\) the calculated LOQ concentration is given by:

\[
\text{Concentration} = \frac{\text{LOQ}}{\text{peak area}/x}
\]

(Equation 5.3)
As an example, a 500 µg l\(^{-1}\) atrazine sample (tab 142)

Peak area = 70186 and reported signal to noise = 16786

\[
\text{RMS}_{\text{noise}} = \frac{70186}{16786} = 4.181 \text{ and therefore}
\]

\[
\text{LOD} = 3 \times \text{RMS}_{\text{noise}} = (3 \times 4.181) = 12.54
\]

\[
\text{LOD concentration} = \frac{12.54}{(70186/500)} = 0.089 \text{ µg l}^{-1}
\]

\[
\text{LOQ} = 10 \times \text{RMS}_{\text{noise}} = (10 \times 4.181) = 41.81
\]

\[
\text{LOQ concentration} = \frac{41.81}{(70186/500)} = 0.298 \text{ µg l}^{-1}
\]

### 5.4.3 Method Detection Limits

Method Detection Limits (MDL) were calculated according to EPA 40 CFR 136 [8] which states that the MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and determined from analysis of a sample in a given matrix containing the analyte and the minimum number of samples needed to calculate the MDL is 7. The MDL is then given as:

\[
\text{MDL}_{\text{conc.}} = \frac{\text{(sample standard deviation) \times (student } t\text{’ value)}}{\text{(mean signal / sample concentration)}}
\]

(Equation 5.4)

As an example for a 500 µg l\(^{-1}\) atrazine sample \((n = 8)\) (the student \(t\)-test value used is \(n\) minus 1 =7 and therefore from Table 5.4 the \(t\)’value is 2.998).

\[
\text{MDL}_{\text{conc.}} = \frac{(1557.64) \times (2.998)}{(72679 / 500)}
\]

\[
\text{MDL}_{\text{conc.}} = 32.1 \text{ µg l}^{-1}
\]
Table 5.4 Single-sided Student’s t-values for 99% confidence limits

| Degree of freedom | 99%    |
|-------------------|--------|
| 1                 | 31.82  |
| 2                 | 6.965  |
| 3                 | 4.541  |
| 4                 | 3.747  |
| 5                 | 3.365  |
| 6                 | 3.143  |
| 7                 | 2.998  |
| 8                 | 2.896  |
| 9                 | 2.821  |
| 10                | 2.764  |

5.5 Investigation 1: Five Day Sample Stability Study

To investigate the reproducibility of peak area response based on the first MS/MS transition, a series of intraday (n=8) and interday (n=5) analyses were conducted to test the sample variability over a period of five days.

A mixture of the seventeen analytes listed in Table 1.2 was prepared in HQ water to produce a standard synthetic matrix to simulate these compounds in water. The matrix was made up at a concentration of 1000 \( \mu \text{g l}^{-1} \). From this, a series of dilutions were prepared to give calibration standards at 10 \( \mu \text{g l}^{-1} \), 50 \( \mu \text{g l}^{-1} \), 100 \( \mu \text{g l}^{-1} \), 250\( \mu \text{g l}^{-1} \), 500 \( \mu \text{g l}^{-1} \), 750 \( \mu \text{g l}^{-1} \) and 1000 \( \mu \text{g l}^{-1} \).

Peak area responses for eight repeat measurements per analyte at each concentration were recorded for five days. The peak area response was recorded for the first and second ion transitions, the second only for confirmation purposes of individual analyte presence.
Figure 5.10 shows an example calibration curve of atrazine, propazine and isoproturon over the seven concentrations showing the linearity of the calibration curves. A similar graph was produced for each individual compound (see Appendix 2 Figures B1 to B17).

![Calibration Curve Example](image)

**Figure 5.10** An example of the reproducibility results of three analytes (atrazine, propazine and isoproturon)

Table 5.5 shows an example of the peak area response reporting from MassLynx for the atrazine compound indicated in Figure 5.10. The calibration curves in Appendix 2 B1 to B17 were produced based upon similar peak area response data for each individual compound.

In Table 5.5 the ‘Detection Flag’ indicates which samples are included in the analyses, samples marked ‘bb’ are included whilst excluded points are marked with bbX. The MassLynx software attempts to identify which measurement results are outside set limits however because of systematic instrument errors the data points which are flagged cannot be dismissed.
### Table 5.5: Example of the Peak Area reporting of repeat measurements for atrazine concentrations over 5 days generated by the MassLynx software

| Concentration | ATR | day01 | day02 | day03 | day04 | day05 |
|---------------|-----|-------|-------|-------|-------|-------|
| (μg l⁻¹)      |     |       |       |       |       |       |
| 10            |     |       |       |       |       |       |
| 50            |     |       |       |       |       |       |
| 100           |     |       |       |       |       |       |
| 250           |     |       |       |       |       |       |
| 500           |     |       |       |       |       |       |
| 750           |     |       |       |       |       |       |
| 1000          |     |       |       |       |       |       |
| 2491.152      | bbX | 29077.63 | 29077.02 | 32608.41 | 32049.87 | 32492.76 |
| 2772.239      | bb  | 13710.88 | 13710.88 | 16038.56 | 15398.89 | 15482.76 |
| 2677.791      | bb  | 14731.49 | 27363.27 | 26369.87 | 25839.89 | 26042.76 |
| 2569.556      | bb  | 14668.74 | 27060.69 | 26862.41 | 26192.89 | 26302.76 |
| 2613.627      | bb  | 14428.83 | 29338.28 | 29760.87 | 29239.89 | 29352.76 |
| 3003.73       | bbX | 13506.45 | 30520.83 | 30060.87 | 29539.89 | 29652.76 |
| 2682.614      | bb  | 14014.11 | 29984.49 | 29760.87 | 29239.89 | 29352.76 |
| 2714.975      | bb  | 14694.68 | 16486.74 | 16038.56 | 15398.89 | 15482.76 |
| 3012.749      | bbX | 17359.96 | 31999.02 | 31269.87 | 30739.89 | 30852.76 |
| 3258.345      | bb  | 20841.01 | 32450.34 | 31608.56 | 31078.89 | 31191.76 |
| 3214.067      | bb  | 16670.9  | 32271.02 | 31428.56 | 30898.89 | 31011.76 |
| 3060.69       | bb  | 16386.47 | 33336.73 | 32486.56 | 31956.89 | 32079.76 |
| 3267.953      | bb  | 16098.42 | 31684.41 | 30834.56 | 30304.89 | 30427.76 |
| 3042.157      | bb  | 17008.11 | 32264.38 | 31414.56 | 30884.89 | 30997.76 |
| 2470.158      | bbX | 16495.71 | 32495.06 | 31645.56 | 31115.89 | 31228.76 |
| 3148.37       | bb  | 16590.41 | 31829.74 | 31079.56 | 30549.89 | 30662.76 |
| 3098.144      | bb  | 15314.13 | 32740.87 | 32090.56 | 31560.89 | 31673.76 |
| 3397.059      | bbX | 15410.56 | 32070.69 | 31320.87 | 30790.89 | 30903.76 |
| 3156.663      | bb  | 16072.76 | 32611.51 | 31861.56 | 31331.89 | 31444.76 |
| 3073.368      | bb  | 15413.61 | 32116.18 | 31361.56 | 30831.89 | 30944.76 |
| 3063.138      | bb  | 14947.48 | 31117.61 | 30361.56 | 29831.89 | 29944.76 |
| 3057.406      | bb  | 17012.47 | 32669.12 | 31919.56 | 31389.89 | 31502.76 |
| 3028.865      | bb  | 17322.24 | 31828.16 | 31078.56 | 30548.89 | 30661.76 |
| 3025.015      | bb  | 15859.27 | 32594.55 | 31844.56 | 31314.89 | 31427.76 |
| 1899.078      | bb  | 13329.87 | 32740.87 | 32090.56 | 31560.89 | 31673.76 |
| 1298.515      | bbX | 13445.35 | 32070.69 | 31320.87 | 30790.89 | 30903.76 |
| 1566.307      | bbX | 14209.3  | 32611.51 | 31861.56 | 31331.89 | 31444.76 |
| 2033.007      | bb  | 14299.56 | 32116.18 | 31466.56 | 30936.89 | 31049.76 |
| 2405.195      | bb  | 14285.24 | 31117.61 | 30361.56 | 29831.89 | 29944.76 |
| 2627.12       | bb  | 14216.56 | 32669.12 | 31919.56 | 31389.89 | 31502.76 |
| 2684.9        | bb  | 14012.79 | 31828.16 | 31078.56 | 30548.89 | 30661.76 |
| 2436.019      | bb  | 13700.47 | 32594.55 | 31844.56 | 31314.89 | 31427.76 |
| 3080.721      | bb  | 16516.63 | 34427.6  | 33833.719 | 33242.76 | 33552.76 |
| 2709.136      | bbX | 17033.85 | 33712.02 | 33122.87 | 32532.89 | 32645.76 |
| 2962.203      | bb  | 16910.58 | 34415.46 | 33845.89 | 33255.89 | 33568.76 |
| 3412.2        | bb  | 16645.9  | 32647.15 | 32059.89 | 31472.89 | 31585.76 |
| 3162.744      | bb  | 17181.51 | 34462.33 | 33845.89 | 33255.89 | 33568.76 |
| 3519.969      | bbX | 17075.8  | 33850.25 | 33242.76 | 32655.89 | 32768.76 |
| 3150.511      | bb  | 17358.21 | 33543.74 | 32963.23 | 32375.89 | 32488.76 |
| 3041.108      | bb  | 16592.56 | 33743.82 | 33146.45 | 32559.89 | 32672.76 |

Note: Concentrations are reported in μg l⁻¹.
5.5.1 Investigation 1 Results

The data from Table 5.5 for atrazine and the other sixteen compounds was used to produce the Figures D1 to D51 in Appendix 2 which show the peak area response all compounds across the full range of concentrations at 10, 500, 1000 µg l\(^{-1}\) (n=8) in the five day reproducibility study. On each figure, the mean value of readings is shown along with two and three standard deviations above and below the mean (±2σ and ±3σ).

The ±2σ and ±3σ limits are chosen as indicating values to be within acceptable parameters of the mean following the Shewhart control chart according to Analytical Methods Committee Technical Brief from the Royal Society of Chemistry [9].

If the compounds under investigation were degrading or deteriorating over the period of the trial, the day to day results would indicate this by showing the peak area response declining from the first to the last day. Figure 5.11 show the 5 day (n=8) reproducibility study example of simazine\(_{d10}\) at 500 µg l\(^{-1}\) concentration.

![Five day reproducibility study - Simazine\(_{d10}\) (500 µg l\(^{-1}\)) n = 8](image)

**Figure 5.11** Five day reproducibility study for simazine\(_{d10}\) at 500 µg l\(^{-1}\)
The results from all the 10 µg l\(^{-1}\) studies indicates that the peak area response of all compounds was ±2σ for all compounds except for isoproturon\(_{d6}\) and diuron \(_{d6}\). For both these compounds the first injection on day five gave peak area response outside 3σ (outside -3σ for isoproturon\(_{d6}\) and +3σ for diuron\(_{d6}\)). By applying the Grubbs Test for Outliers [10] it is shown that these two plots can be classed as outliers. For the compound alachlor\(_{d13}\), replicate three and six on day six fell outside -2σ but were above -3σ level.

However on day four, the first four replicate injections does show a reduced peak area response for all the compounds, the response is lower and falls to approximately -3σ. As this pattern is followed by every compound, it is an indication that an instrument problem occurred during the first four injections. This pattern was not repeated on any other day and at no other concentration.

Observing the peak areas response of all compounds at 500 µg l\(^{-1}\) concentration, it can be seen that most of the readings fall between the upper and lower ±2σ level. However for atrazine, isoproturon, simazine, cyanazine, chlortoluron and linuron one replicate of each fell outside the -2σ but within 3σ level.

The day to day readings indicate that there is no reduction in peak area response from the day to day readings which indicate that that no degradation or deterioration of the compounds under investigation occurred. From the figures it can be seen that day one peak area response for all compounds except alachlor, isoproturon\(_{d6}\), diuron\(_{d6}\) and alachlor\(_{d13}\) was below the other four days but still within the 2σ.

The peak area response for all compounds at 1000 µg l\(^{-1}\) were within the ±2σ except for isoproturon day four replicate three which was still within 3σ. Atrazine day 1 replicate 4 and
chlortoluron day 1 replicate 4 both fell outside -2σ but both are classed as outliers according to Grubbs test for outliers.

The day to day peak area peak area response showed no signs of compound degradation for all compounds except simazine_d10 and cyanazine. Whilst the peak area response for both fell within ±2σ, and cyanazine actually fell within one standard deviation of the mean, the signal from day to day was reduced.

5.5.2 Summary of Results

Data from this investigation indicates that for most compounds at most concentrations, there is no loss of signal due to storage of samples over the five day period of the study. At the 10 µg l⁻¹ concentration the results from the 5 days show that there is no peak area signal response reduction and therefore no loss of analyte over the trial period of 5 days. At 500 and 1000 µg l⁻¹ concentrations again there is no discernable signal loss and therefore no compound degradation over the trial period except for cyanazine and simazine_d10.

As an example, the daily mean peak area response for atrazine at 750 µg l⁻¹ is shown in Table 5.6. The %RSD for all the compounds at each concentration was below 20 and for most concentrations the value was below 10 and in many cases below 5. The average %RSD for atrazine for each concentration over the five days was 3.8.

Table 5.7 shows the R² values obtained from the 5 day peak area signal reproducibility studies for all analytes.
Table 5.6 Peak area response (n = 8) for atrazine (750 µg l⁻¹) over five days

| Day | Peak area response of atrazine at 750 µg l⁻¹ (n=8) |
|-----|--------------------------------------------------|
| 1   | 182610                                           |
| 2   | 200544                                           |
| 3   | 196487                                           |
| 4   | 185524                                           |
| 5   | 185953                                           |
| mean| 190223                                           |
| sd  | 7810                                             |
| %RSD| 4.1                                              |

Table 5.7 Calculated R² average values for 5 day reproducibility study

| Compound              | R²  |
|-----------------------|-----|
| Atrazine              | 0.989|
| Propazine             | 0.991|
| Isoproturon           | 0.995|
| Diuron                | 0.996|
| Atr-desisopropyl      | 0.991|
| Atr-desethyl          | 0.991|
| Simazine              | 0.994|
| Cyanazine             | 0.993|
| Alachlor              | 0.994|
| Chlortoluron          | 0.990|
| Linuron               | 0.995|
| Atrazine_d₃           | 0.988|
| Propazine-2-hydroxy   | 0.990|
| Isoproturon_d₆        | 0.992|
| Diuron_d₆             | 0.988|
| Simazine_d₁₀          | 0.985|
| Alachlor_d₁₃          | 0.992|
5.6 Investigation 2: Seven Day Instrument Interday Variation Study

The second investigation was to study the reproducibility (n=6) of peak area response based on the first MS/MS transition, a series of interday (n=7) analyses were conducted to test the instrument variability over a period of seven days. A fresh mixture of all seventeen compounds was prepared at a concentration of 100 μg l⁻¹ each day for seven days in HQ water. Over the study period, an injection was made daily of the fresh sample and monitored for the primary and secondary ion transition. Table 5.8 shows an example of the reporting format spreadsheet.

**Table 5.8** Example reporting spreadsheet for one of the compounds analysed (atrazine)

| 10_Day01 |
| --- |
| Compound 1: ATRAZINE |
| Name | RT | Area | Sec.Area |
| 10_07_08_day01_100ugL_01 | 4.25 | 20239.7 | 6007.8 |
| 10_07_08_day01_100ugL_02 | 4.25 | 18485.4 | 5718.2 |
| 10_07_08_day01_100ugL_03 | 4.27 | 20268.0 | 5883.3 |
| 10_07_08_day01_100ugL_04 | 4.25 | 20544.8 | 6086.3 |
| 10_07_08_day01_100ugL_05 | 4.25 | 21948.4 | 6302.7 |
| 10_07_08_day01_100ugL_06 | 4.25 | 22298.0 | 6265.1 |
| mean | 4.25 | 20630.7 | 6043.9 |
| std | 1252.4 | 189.3 |
| %rsd | 6.07 | 3.13 |
| n= | 6 | 6 |

Where
- Name = MassLynx data file name.
- RT = Sample retention time (in minutes).
- Area = 1st transition peak area.
- Sec.Area = 2nd transition peak area.

The report calculates the mean peak area for the replicates for the first transition and second transitions, the standard deviation for each transition across the replicates and the associated %RSD.
5.6.1 Investigation 2 Results

Figure 5.12 graphically shows the peak area response (n=6) for atrazine over the seven day period. All 17 compounds are recorded in appendix 2 C1 to C17. Table 5.9 shows the mean peak area response (n=7) for the primary and secondary transitions of all compounds over the seven day period.

Figure 5.13 shows, as an example, the mean peak area response (n=6) for primary transition of atrazine (100 µg l$^{-1}$) over seven days showing 2 and 3 standard deviation limits above and below the mean. The mean peak area response (n=6) for primary transitions of all seventeen compounds for 7 days at 100 µg l$^{-1}$ are shown in Appendix 2 E.1 to E.17.

![Figure 5.12](image_url)

**Figure 5.12** The series of reproducibility results for the analytes and standards showing both transitions. The error bars represent one standard deviation.
Figure 5.13  Mean peak area response for primary transition of atrazine (100 µg l\(^{-1}\)) over seven days showing ±2σ and ±3σ

Figure 5.14  Mean peak area response for primary transition of linuron (100 µg l\(^{-1}\)) over seven days showing ±2σ and ±3σ

It can be seen from Figure 5.13 that the first transition mean peak area response, over the seven days for atrazine falls between ±2σ. The same is observed for all other sixteen compounds with the first transition mean peak area response, over the seven days falling
between ±2σ. Isoproturon, diuron, alachlor, linuron, an example of which is linuron in Figure 5.14, all show a reading close to the mean on day seven. This would indicate that there is no general trend of the mean peak area response and therefore compound concentrations to reduce over the course of the seven day trial period. Most compounds show that the day one mean peak area response is the highest of all readings for each compound, this may indicate a systematic error. There were a number of readings on day seven for diuron-d₆, simazine-d₁₀, hydroxypropazine as well day one reading for propazine which were calculated to be outliers according to Grubbs’ test for outliers. This again could indicate a systematic error.

**Table 5.9** Mean peak area response for the primary and secondary transitions for all 17 compounds over 7 days at 100 µg l⁻¹

| Compound              | Molecular ion [M+H]⁺ | Primary ion | Secondary ion |
|-----------------------|----------------------|-------------|---------------|
|                       | Ion transition       | Mean peak area response (n=7) | Standard deviation | %RSD | Ion transition | Mean peak area response (n=7) |
| Atrazine              | 216.2                | 174.1       | 15917         | 836.9 | 5.2           | 95.6              | 4659 |
| Propazine             | 230.1                | 146.0       | 7156          | 1178.4 | 23.6          | 188.1             | 4839 |
| Isoproturon           | 207.1                | 165.1       | 1108          | 79.5   | 7.1           | 134.0             | 126  |
| Diuron                | 233.0                | 72.0        | 371           | 25.4   | 7.0           | 159.9             | 50   |
| Atrazine desisopropyl | 174.1                | 95.9        | 725           | 64.0   | 9.0           | 132.2             | 808  |
| Atrazine desethyl     | 188.1                | 146.0       | 4163          | 289.8  | 7.3           | 103.9             | 917  |
| Simazine              | 202.4                | 124.1       | 4370          | 227.6  | 5.3           | 132.1             | 4512 |
| Cyanazine             | 241.5                | 214.2       | 1563          | 71.7   | 4.6           | 96.0              | 416  |
| Alachlor              | 270.0                | 238.0       | 409           | 11.8   | 13.2          | 162.0             | 93   |
| Chlortoluron          | 213.0                | 72.0        | 1384          | 90.3   | 7.1           | 140.0             | 120  |
| Linuron               | 249.0                | 160.0       | 298           | 28.5   | 10.0          | 182.0             | 195  |
| Atrazine_d₅           | 221.2                | 178.9       | 6061          | 407.7  | 7.3           | 100.7             | 1620 |
| Propazine-2-hydroxy   | 212.3                | 127.7       | 6812          | 375.2  | 10.9          | 169.9             | 3922 |
| Isoproturon_d₆        | 213.3                | 77.6        | 1389          | 102.1  | 9.5           | 133.8             | 134  |
| Diuron_d₆             | 239.2                | 77.5        | 207           | 20.1   | 12.3          | 159.7             | 37   |
| Simazine_d₁₀          | 212.2                | 136.7       | 2649          | 160.2  | 9.8           | 133.8             | 2788 |
| Alachlor_d₁₃          | 283.3                | 250.9       | 183           | 25.4   | 16.4          | 175.0             | 139  |
5.6.2 Summary of Results

Table 5.9 shows the mean peak area response of the primary and secondary ion transition for the 17 analytes measured over 7 days at a concentration of 100 µg l⁻¹. The primary transition ion peak area responses are used for quantification while the secondary ion transitions are used for confirmatory purposes only.

Comparing the primary and secondary peak area responses for atrazine desisopropyl \((1^0 = 725 / 2^0 = 808)\), simazine \((1^0 = 4370 / 2^0 = 4512)\) and simazine \(\text{d}_{10} \ (1^0 = 2649 / 2^0 = 2788)\) the second transition peak areas are very similar but slightly greater than the first ion transition. This is not an error but occurs when more than one analyte and therefore the second ion transition chosen for confirmatory purposes were not always be the most intense ion transition.

The average peak area response for all 17 analytes was 3221 with an average %RSD of 9.7% but there was a wide range of sensitivities between individual analytes. The three largest mean peak area responses were for atrazine (15917), propazine (7156) and propazine-2-hydroxy (6812). The three lowest mean peak area responses were for alachlor\(_{\text{d}_{13}}\) (183), diuron\(_{\text{d}_{6}}\) (207) and linuron (298). Whilst the good average %RSD was 9.7%, examining all the analytes there was a range from lowest to highest. The three lowest were cyanazine (4.6%), atrazine (5.2%) and simazine (5.3) and the three highest alachlor (13.2), alachlor\(_{\text{d}_{13}}\) (16.4) and propazine 23.6).

From the Figures in Appendix 2 E.1 to E.17 the general trend of the mean peak area responses of the compounds under investigation does not indicate that there is no significant
loss of compound concentration as the signals do not fall outside the two standard deviations from the mean and that no signal fall outside three standard deviations from the mean.

5.7 Investigation 3: Investigation of analyte loss during extraction

Investigation 3 introduces the filtration and SPE extraction steps into the study to determine the analytes losses due to filtration of samples to remove solid particulates from the river water matrix and from analyte losses in the SPE cartridge.

Source water from the River Ogmore was filtered to remove particulates and extracted by SPE and was spiked with the 17 compound mixture (500 µg l⁻¹) either pre or post filtering and extraction. These were then analysed using the optimised chromatographic method mei128. The analyses of the River Ogmore (Bwlch Mountain) results allowed the quantification of the analyte losses in river water samples due to the filtration and extraction.

Post extraction sample: A one litre sample of source water was filtered and extracted by SPE. To this, a standard of all 17 compounds at 500 µg l⁻¹ was added.

Pre extraction sample: To a second one litre sample, the same 17 compound standard was added and then filtered and extracted by SPE.

Tab numbers on the following tables and figures refer to the data stored electronically. Table 5.10 shows the mean peak area results for post extraction spiked samples (tab 142) and pre spiked samples (tab 145) from which the analyte losses through filtration and SPE are calculated. Using the data from the two spiked samples it was possible to calculate the instrumental limits of detection and quantification. Figure 5.15 displays graphically the pre and post spiked results (tab 142 / tab 145).
Table 5.10  Investigation 3: The mean peak area response and instrumental LOD and LOQ calculated from spiked River Ogmore (Bwlch)

| Compound number | Analyte               | TAB145 (analytes added before SPE) | TAB142 (analytes after SPE) | % recovery based on mean peak area (tab142/tab 145) |
|-----------------|-----------------------|------------------------------------|----------------------------|---------------------------------------------------|
|                 |                       | Mean Peak Area (n = 8)              | Avg LOD* (µg l⁻¹)          | Avg LOQ* (µg l⁻¹)                                  |
|                 |                       | Mean Peak Area (n = 8)              | Avg LOD* (µg l⁻¹)          | Avg LOQ* (µg l⁻¹)                                  |
| 1               | ATRAZINE              | 53927                              | 0.12                       | 0.39                                              | 72679                              | 0.05                       | 0.18                       | 74.2                                             |
| 2               | PROPZINE              | 31057                              | 0.19                       | 0.62                                              | 48734                              | 0.11                       | 0.37                       | 63.7                                             |
| 3               | ISOPROTURON           | 8525                               | 0.59                       | 1.96                                              | 11287                              | 0.51                       | 1.71                       | 75.5                                             |
| 4               | DIURON                | 34                                 | 35.52                      | 118.38                                            | 161                                | 13.19                      | 43.97                      | 21.3                                             |
| 5               | ATR-DESISOPROPYL      | 6041                               | 0.42                       | 1.39                                              | 7813                               | 0.34                       | 1.14                       | 77.3                                             |
| 6               | ATR-DESETHYL          | 42392                              | 0.30                       | 0.98                                              | 55980                              | 0.22                       | 0.74                       | 75.7                                             |
| 7               | SIMAZINE              | 25525                              | 0.15                       | 0.51                                              | 31615                              | 0.19                       | 0.62                       | 80.7                                             |
| 8               | CYANAZINE             | 11169                              | 0.71                       | 2.36                                              | 13372                              | 0.64                       | 2.14                       | 83.5                                             |
| 9               | ALACHLOR              | 268                                | 41.75                      | 139.15                                             | 665                                | 30.82                      | 102.75                     | 40.2                                             |
| 10              | CHLORTOLURON          | 4872                               | 0.42                       | 1.41                                              | 8612                               | 0.27                       | 0.89                       | 56.6                                             |
| 11              | LINURON               | 1                                  | 299.72                     | 999.08                                             | 3                                  | 220.71                     | 735.70                     | 40.2                                             |
| 13              | HYDROXYPROPAZINE      | 110923                             | 0.05                       | 0.16                                              | 136158                             | 0.08                       | 0.25                       | 81.5                                             |
|                 |                       | Set 1 deuterated standards         |                            |                                                   |                                    |                            |                            |                                                   |
| 14              | ISOPROTURON_d6        | 15428                              | 0.26                       | 0.86                                              | 20140                              | 0.31                       | 1.02                       | 76.6                                             |
| 16              | SIMAZINE_d10          | 31497                               | 1.84                       | 6.14                                              | 38637                              | 0.81                       | 2.70                       | 81.5                                             |
| 17              | ALACHLOR_d13          | 156                                | 42.33                      | 141.09                                             | 416                                | 21.94                      | 73.12                      | 37.6                                             |
|                 |                       | Set 2 deuterated standards         |                            |                                                   |                                    |                            |                            |                                                   |
| 12              | ATRAZINE_d5           | 30393                              | 0.20                       | 0.67                                              | 43142                              | 0.12                       | 0.42                       | 70.4                                             |
| 15              | DIURON_d6             | 30                                 | 25.57                      | 85.25                                              | 128                                | 7.15                       | 23.85                      | 23.4                                             |

* Calculated as outlined in Section 5.4.2
Figure 5.15 River Ogmore source water percentage recovery of analytes described in Table 5.10 post (Tab 142) and pre (Tab 145) extraction spiked water comparison

5.7.1 Summary of results

Analytes added to source river water before and after particulate filtration and SPE samples had an average percentage recovery for all 17 compounds of 62.4% with highest being cyanazine (83.5%) and diuron (21.3%). The average peak area response for all compounds for samples spiked before particulate filtration and SPE was 28797 against 23264 for post spiked samples with highest response for pre spiked samples being hydroxy-2-propazine (136158) and the lowest, diuron (161).

The average LOD for spiked samples before particulate filtration and SPE was 4.80 µg l⁻¹ and the LOQ 15.99 µg l⁻¹ whilst for samples spiked after particulate filtration and SPE the average LOD was 9.4 µg l⁻¹ and an LOQ of 31.3 µg l⁻¹.
The LOD for spiked samples before particulate filtration and SPE fell between 30.8 µg l\(^{-1}\) for alachlor and 0.05 µg l\(^{-1}\) for atrazine. The LOQ alachlor was 102.7 µg l\(^{-1}\) and 0.18 µg l\(^{-1}\) for atrazine. The spiked samples after particulate filtration and SPE showed an LOD range of between 41.7 µg l\(^{-1}\) for alachlor and 0.12 µg l\(^{-1}\) for atrazine.

5.8 Investigation 4: Determination of concentration of target analytes in river water

Investigation 4 determined the concentration of the 12 compounds in the River Wye, River Ogmore and River Ely at various sampling points along the river course. Table 5.11 describes the sampling point, description of the sampling point, date sampled and under the Run column, the tab number of each sample. Each tab number is a separate sample of river water.

For each run, one litre sample of river water was sampled, pH adjusted and spiked with ‘Set 1’ internal deuterated standards of isoproturon\(_{d_6}\), simazine\(_{d_{10}}\) and alachlor\(_{d_{13}}\). Each sample was then filtered and extracted, evaporated to dryness and reconstituted in 1 cm\(^3\) of initial mobile phase to which ‘Set 2’ internal standards of atrazine\(_{d_5}\), and diuron\(_{d_6}\) was added.

Tables 5.12 to Table 5.23 shows the compound name, ‘Set 1 and Set 2 internal standards (IS), mean peak area response (n=8), standard deviation (std. dev.), %RSD, % of the MDL and calculated concentration in µg l\(^{-1}\) for each tab number which relates to each sample as described in Table 5.11. The percentage MDL for each analyte must be 100% before the data can be used with confidence as described in Section 5.4.2.

Figure 5.16 shows the combined results from Tables 5.12 to 5.16 for each of the compounds under investigation in the River Wye. The results are calculated as a percentage of the determined analyte against the MDL for that compound. Similarly Figure 5.17 shows the
combined results for Tables 5.17 to 5.21 for the River Ogmore and Figure 5.18 shows the combined results for Tables 5.22 to 5.23 for the River Ely.
### Table 5.11  Summary of the rivers studied including sampling points measured, run number and table of results

| River               | Sampling Point                  | Description              | Dates Sampled   | Runs                     | Results Table Number |
|---------------------|---------------------------------|---------------------------|-----------------|--------------------------|----------------------|
| Wye                 | Newbridge-on-Wye                | Close to source           | 14 July 2009    | Tab 107 : Tab 108        | Table 5.12           |
|                     | Llangerig                       | Rural                     | 8 May 2009      | Tab 30 : Tab 31          | Table 5.13           |
|                     |                                 |                           | 15 May 2009     | Tab 135 : Tab 138        |                      |
|                     | Kerne Bridge                    | Rural / City influence    | 15 Jul 2009     | Tab 172 : Tab 175 : Tab 176 | Table 5.14           |
|                     |                                 |                           |                 | Tab 177 : Tab 180 : Tab 183 | Table 5.15           |
|                     | Symonds Yat                     | Rural / City influence    | 8 May 2009      | Tab 32 : Tab 33          | Table 5.16           |
|                     |                                 |                           | 14 May 2009     | Tab 110 : Tab 113        |                      |
| Ogmore              | Bwlch Mountain                  | Close to source           | 14 Jul 2009     | Tab 40 : Tab 142 : Tab 145 | Table 5.17           |
|                     |                                 |                           |                 | Tab 143 : Tab 146 - Tab 148 |                      |
|                     | New Mill                        | Rural                     | 14 Jul 2009     | Tab 152 : Tab 153 : Tab 155 | Table 5.18           |
|                     |                                 |                           |                 | Tab 156 : Tab 157 : Tab 158 | Table 5.19           |
|                     | Ogmore Castle (below treatment works) | Rural / City influence | 14 Jul 2009 | Tab 160 : Tab 162 : Tab 163 | Table 5.20           |
|                     |                                 |                           |                 | Tab 164 : Tab 165 : Tab 166 : Tab 167 | Table 5.21           |
| Ely                 | Thomastown                      | Close to source           | 8 May 2009      | Tab 115                  | Table 5.22           |
|                     | Ely Valley                      | Rural                     | 8 May 2009      | Tab 116                  | Table 5.22           |
|                     | Peterston/Super Ely             | Rural                     | 8 May 2009      | Tab 120 : Tab 121        | Table 5.22           |
|                     | St. Georges                     | Rural                     | 8 May 2009      | Tab 122 : Tab 123        | Table 5.23           |
|                     | Llancafarn (Thaw)               | Rural                     | 8 May 2009      | Tab 117                  | Table 5.23           |
Table 5.12 River Wye water samples showing mean peak area response and MDL and reportable concentration for each compound

| WYE          | Grid Ref: N52.21360 W3.47083 |
|-------------|-------------------------------|
| **Newbridge-on-Wye (14 July 2009)** |                              |
| Analyte     | Mean Peak Area | Std Dev | % RSD | Mean % signal | Tab 106 spiked sample 500 µg/L | TAB107 Sample 0.02 µg/L | Mean % signal | Tab 108 Sample 0.02 µg/L | Mean Peak Area | Std Dev | % RSD | % of MDL |
| DIURON_d6   | 4322            | 98.51%  | 2.23% | 3052           | 18.29                        | 30.38%                    | 0.96%                       | 928.65          | 95.81% | 1.22% | 0.32%  |
| ALACHLOR_d13| 2900            | 343.07% | 1.71% | 1029           | 2.49                         | 48.67%                    | 1.22%                      | 10039.36        | 26.97% | 0.85% | 429.28% |
| SIMAZINE    | 19123           | 451.70% | 2.36% | 417            | 5.58                         | 30.50%                    | 1.11%                       | 51928.95        | 20.57% | 0.77% | 20.57% |
| Desisopropyl| 18315           | 446.87% | 1.56% | 31             | 1.21                         | 22.35%                    | 0.78%                       | 53805.35        | 19.72% | 0.65% | 19.72% |
| ATRAZINE    | 51661           | 1369.26%| 2.46% | 10039.36       | 10039.36                    | 13.50%                    | 3.89%                       | 10039.36        | 70.94% | 17.35% | 4.75%  |
| LINURON     | 3052            | 69.56%  | 2.28% | 6767           | 35.15                        | 85.00%                    | 0.96%                       | 149078          | 6.73%  | 0.32% | 6.73%  |

Table 5.13 River Wye water samples showing mean peak area response and MDL and reportable concentration for each compound

| Llangollen (8 May 2009) | TAB30 Sample 0.01 µg/L | TAB31 Sample 0.01 µg/L |
|-------------------------|------------------------|------------------------|
| Analyte number          | Analyte                | Mean Peak Area | Std Dev | % RSD | % of MDL | (µg l⁻¹) | Mean Peak Area | Std Dev | % RSD | % of MDL | (µg l⁻¹) |
| 1                       | ATRAZINE               | 4.28                | 3.85%  | 90%   | 0.07%   | 0.01%     | 3.71               | 3.15% | 85%   | 0.06%   | 0.01%     |
| 2                       | PROPZINE               | 5.03                | 3.75%  | 75%   | 0.07%   | 0.01%     | 2.88               | 5.05% | 87%   | 0.04%   | 0.01%     |
| 3                       | ISOPROTURON            | 3.35                | 3.35%  | 100%  | 0.51%   | 0.01%     | 13.57              | 13.48%| 99%   | 0.25%   | 0.30%     |
| 4                       | DIURON                 | 1.95                | 1.04%  | 53%   | 0.67%   | 0.12%     | 2.56               | 1.95% | 76%   | 0.88%   | 0.30%     |
| 5                       | ATR-DESISOPROPY        | 1.73                | 1.85%  | 107%  | 1.21%   | 0.33%     | 3.21               | 3.56% | 111%  | 2.25%   | 0.62%     |
| 6                       | ATRA-DESETHYL          | 4.36                | 5.28%  | 121%  | 0.33%   | 0.10%     | 3.05               | 2.67% | 88%   | 0.23%   | 0.07%     |
| 7                       | SIMAZINE               | 1.50                | 1.41%  | 94%   | 0.11%   | 0.04%     | 2.11               | 2.49% | 118%  | 0.16%   | 0.06%     |
| 8                       | CYANAZINE              | 1.15                | 1.79%  | 156%  | 0.23%   | 0.10%     | 1.83               | 2.40% | 131%  | 0.37%   | 0.16%     |
| 9                       | ALACHLOR              | 1.65                | 1.98%  | 120%  | 0.40%   | 0.12%     | 1.67               | 2.09% | 125%  | 0.40%   | 0.12%     |
| 10                      | CHLORTOLURON          | 2.76                | 2.19%  | 79%   | 0.27%   | 0.07%     | 4.77               | 6.23% | 131%  | 0.46%   | 0.12%     |
| 11                      | LINURON               | 2.51                | 2.22%  | 88%   | 1.46%   | 0.49%     | 0.85               | 0.66% | 77%   | 0.50%   | 0.17%     |
| 12                      | HYDROXYPROPZINE        | 5.28                | 3.42%  | 65%   | 0.17%   | 0.05%     | 6.16               | 4.53% | 73%   | 0.20%   | 0.06%     |

Where: mean peak area n = 8
Column heading - MDL signal = mean peak area signal response
Column heading - MDL ug l\(^{-1}\) = MDL concentration in µg l\(^{-1}\)
Column heading - ug l\(^{-1}\) = actual reportable concentrations

Source water (Tab106 Table 5.12) was used to determine %MDL
Table 5.14 River Wye water samples showing mean peak area response and MDL and reportable concentration for each compound

| Analyte               | TAB172 unspiked | TAB175 unspiked | TAB176 unspiked |
|-----------------------|-----------------|-----------------|-----------------|
|                       | Mean Area       | Std Dev         | % RSD           | % of MDL | Mean Peak Area   | Std Dev         | % RSD           | % of MDL |
| ATRAZINE              | 26              | 24.49           | 9.42%           | 4.14%    | 210              | 22.59           | 10.78%          | 3.34%   |
| PROPANE               | 13              | 4.52            | 34.17%          | 0.20%    | 13               | 10.76           | 81.56%          | 0.20%   |
| ISOPROTURON           | 53              | 38.94           | 73.70%          | 8.00%    | 44               | 34.38           | 77.63%          | 6.70%   |
| DIURON                | 18              | 9.05            | 49.72%          | 6.29%    | 12               | 7.37            | 63.13%          | 4.03%   |
| ATR DESISOPROPYL      | 34              | 47.84           | 140.00%         | 23.96%   | 20               | 14.85%          | 18.55%          | 5.07%   |
| ATR DESETHYL          | 46              | 6.63            | 134.00%         | 6.22%    | 44               | 10.76           | 1002.58         | 3.76%   |
| CYANAZINE             | 2               | 1.96            | 92.69%          | 0.43%    | 2                | 1.20            | 54.88%          | 1.35%   |
| ALACHLOR              | 2               | 2.50            | 116.35%         | 0.51%    | 2                | 2.56            | 119.40%         | 0.15%   |
| CHLORTOLURON          | 31              | 9.26            | 30.22%          | 2.98%    | 31               | 9.26            | 109.05%         | 0.45%   |
| LINURON               | 2               | 1.25            | 104.67%         | 0.69%    | 2                | 1.25            | 129.03%         | 0.36%   |
| HYDROXYPROPAZINE      | 22              | 9.98            | 44.94%          | 0.72%    | 16               | 5.42            | 33.73%          | 0.52%   |
| ISOPROTURON_d6        | 33179           | 1340.12         | 4.04%           | 33179    | 1002.58          | 3.76%           | 33179           | 1431.38 |
| SIMAZINE_d10          | 40472           | 4000.18         | 9.88%           | 519.76   | 40472            | 1698.92         | 4.84%           | 5674.27 |
| ALACHLOR_d13          | 3210            | 251.46          | 7.83%           | 6376     | 251.46           | 7.83%           | 3210            | 6376    |

Set 1 % Recovery % Recovery % Recovery
ISOPROTURON_d6 28256 1431.38 5.07% 28256
SIMAZINE_d10 33357 3045.82 9.13% 33357
ALACHLOR_d13 1990 247.08 12.41% 1990

Set 2 Instrument Correction Instrument Correction Instrument Correction
ATRAZINE_d5 125176 7165.09 5.72% 125176 111417 23839.36 21.40% 111417 113716 6276.12 5.52% 113716
DIURON_d6 6376 519.76 8.15% 6376 5674 246.27 4.34% 5674 5069 530.59 10.47% 5069
### Table 5.15  River Wye water samples showing mean peak area response and MDL and reportable concentration for each compound

| Analyte            | Mean Peak Area | Std Dev | % RSD | % of MDL | Mean Peak Area | Std Dev | % RSD | % of MDL | Mean Peak Area | Std Dev | % RSD | % of MDL |
|--------------------|----------------|---------|-------|----------|----------------|---------|-------|----------|----------------|---------|-------|----------|
| ATRAZINE           | 198            | 28.14   | 14.24%| 3.15%    | 238            | 30.98   | 13.03%| 3.79%    | 225            | 14.85   | 6.61%| 3.58%    |
| PROPAZINE          | 6              | 5.43    | 93.67%| 0.09%    | 12              | 5.49    | 46.08%| 0.18%    | 14              | 4.80    | 33.48%| 0.21%    |
| ISOPROTURON        | 30             | 43.42   | 144.96%| 4.53%    | 44              | 39.49   | 90.62%| 6.60%    | 46              | 25.92   | 56.31%| 6.97%    |
| DIUROTRON          | 11             | 5.00    | 47.49%| 3.64%    | 19              | 10.29   | 53.16%| 6.69%    | 13              | 8.52    | 67.96%| 4.34%    |
| ATR-DISOPROPYL     | 24             | 29.09   | 120.25%| 6.61%    | 44              | 26.23   | 41.94%| 6.69%    | 18              | 33.29   | 184.16%| 2.24%    |
| ATR-DESETHYL       | 3              | 2.86    | 60.40%| 0.01%    | 2               | 2.26    | 94.73%| 0.57%    | 2               | 1.74    | 100.92%| 0.24%    |
| ISOPROTURON_d6     | 24             | 1740.88 | 7.22% | 2.80%    | 30522          | 853.94  | 4.64% | 2.80%    | 31454          | 627.00  | 3.61% | 2.80%    |
| SIMAZINE_d10       | 3              | 1315    | 7.37% | 0.80%    | 4126           | 209.28  | 5.07% | 0.80%    | 2765           | 113.75  | 4.11% | 0.80%    |
| ALACHLOR           | 2              | 0.72    | 63.45%| 0.66%    | 2               | 1.74    | 82.66%| 1.23%    | 2               | 2.40    | 107.11%| 0.77%    |
| CHLORTOLURON       | 2              | 63.84% | 0.66% | 0.22%    | 2               | 1.74    | 82.66%| 1.23%    | 2               | 2.40    | 107.11%| 0.77%    |
| HYDROXYPROPAZINE   | 2              | 16.68   | 59.42%| 0.92%    | 25              | 13.72   | 55.70%| 0.80%    | 24              | 11.59   | 48.82%| 0.77%    |

Source water (TAB106 Table 5.12) was used to determine %MDL.
Table 5.16  River Wye water samples showing mean peak area response and MDL and reportable concentration for each compound

| Analyte number | Analyte      | WYE - Symonds Yat East (8 May 2009) |            |            |            |            |            |            |            |            |            |            |            |
|----------------|--------------|-------------------------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
|                |              | Mean Peak Area | Std Dev | % RSD | % of MDL | (µg l⁻¹) | Mean Peak Area | Std Dev | % RSD | % of MDL | (µg l⁻¹) | Mean Peak Area | Std Dev | % RSD | % of MDL | (µg l⁻¹) |
| 1              | ATRAZINE     | 51.63         | 35.79   | 0.69   | 0.82%     | 0.28       | 59.15         | 34.97   | 0.59   |            |            |            |            |
| 2              | PROPAZINE    | 12.40         | 11.78   | 0.95   | 0.18%     | 0.05       | 6.58          | 6.01    | 0.91   |            |            |            |            |
| 3              | ISOPROTURON  | 16.79         | 15.46   | 0.92   | 2.54%     | 0.58       | 14.25         | 12.13   | 0.85   |            |            |            |            |
| 4              | DIURON       | 7.31          | 5.50    | 0.75   | 2.53%     | 0.85       | 5.56          | 3.41    | 0.61   |            |            |            |            |
| 5              | ATR-DESISOPROPYL | 3.62         | 2.89    | 0.80   | 2.54%     | 0.69       | 4.11          | 3.07    | 0.75   |            |            |            |            |
| 6              | ATR-DESETHYL | 17.63         | 14.85   | 0.84   | 1.33%     | 0.42       | 16.51         | 9.88    | 0.60   |            |            |            |            |
| 8              | CYANAZINE    | 9.31          | 6.44    | 0.69   | 0.69%     | 0.24       | 9.12          | 7.37    | 0.81   |            |            |            |            |
| 9              | ALACHLOR     | 2.20          | 1.86    | 0.84   | 0.53%     | 0.16       | 2.20          | 2.10    | 0.95   |            |            |            |            |
| 10             | CHLORTOLURON | 22.07         | 17.57   | 0.80   | 2.15%     | 0.55       | 22.01         | 17.24   | 0.78   |            |            |            |            |
| 11             | LINURON      | 2.61          | 2.11    | 0.81   | 1.52%     | 0.51       | 2.19          | 1.61    | 0.74   |            |            |            |            |
| 13             | HYDROXYPROPZINE | 14.41        | 9.73    | 0.67   | 0.47%     | 0.15       | 9.38          | 3.79    | 0.40   |            |            |            |            |

Source water (Tab16, Table 5.12) was used to determine percentage MDL.

| Analyte number | Analyte      | Mean Peak Area | Std Dev | % RSD | % of MDL | (µg l⁻¹) | Mean Peak Area | Std Dev | % RSD | % of MDL | (µg l⁻¹) |
|----------------|--------------|------------|--------|------|--------|--------|------------|--------|------|--------|--------|
| 12             | ATRAZINE     | 22.27      | 14.89  | 0.67 | 0.67%    | 0.24       | 20.64         | 11.11   | 0.54 |            |            |
| 15             | DIURON       | 4.20       | 2.76   | 0.66 | 0.66%    | 0.28       | 3.85          | 3.07    | 0.80 |            |            |
Figure 5.16 River Wye analyte concentration of the 12 compounds studied expressed as a percentage of the MDL of each compound

Compounds 1 to 13 are identified in Table 5.16 (analyte number)
Table 5.17  River Ogmore water samples showing mean peak area response and MDL and reportable concentration for each compound

| Analyte number | Analyte | Mean Peak Area | Std Dev | % RSD | % of MDL | Mean Peak Area | Std Dev | % RSD | (µg L⁻¹) | Av LOD ug/L | Av LOQ ug/L | Mean Peak Area | Std Dev | % RSD | % Recovery |
|----------------|---------|----------------|---------|-------|----------|----------------|---------|-------|----------|-------------|-------------|-------------|----------------|---------|-------|------------|
| 1              | ATRAZINE| 10.66          | 0.06    | 0.18% | 0.06     | 72679         | 1557.64 | 2.14% | 500      | 0.05        | 0.18        | 53557       | 1189.55       | 201.05  |
| 2              | PROPZINE| 7.59           | 0.03    | 1.05% | 0.03     | 48734         | 892.52  | 1.83% | 500      | 0.11        | 0.37        | 31057       | 391.68         | 201.05  |
| 3              | ISOPROTURON| 14.60       | 1.13    | 7.89% | 1.13     | 11287         | 322.57  | 2.86% | 500      | 0.51        | 1.71        | 85256       | 184.45         | 201.05  |
| 4              | DIURON | 1.93           | 0.23    | 12.41%| 0.23     | 7513          | 169.37  | 2.17% | 500      | 13.19       | 43.97       | 60414       | 201.05         | 201.05  |
| 5              | ATR-DESISOPROPYL| 38.07 | 12.18  | 31.91%| 12.18    | 11287         | 322.57  | 2.86% | 500      | 0.34        | 1.14        | 60414       | 201.05         | 201.05  |
| 6              | ATR-DESETHYL| 258         | 6.14    | 23.83%| 6.14     | 55980         | 896.94  | 1.60% | 500      | 0.22        | 0.74        | 42392       | 3245.11        | 201.05  |
| 7              | SIMAZINE| 2.51           | 0.07    | 2.83% | 0.07     | 31615         | 354.58  | 1.12% | 500      | 0.19        | 0.62        | 25525       | 817.71         | 201.05  |
| 8              | CYANATE| 0.33           | 0.04    | 12.74%| 0.04     | 13372         | 703.24  | 2.66% | 500      | 0.64        | 2.14        | 11169       | 409.49         | 201.05  |
| 9              | LINURON| 1.41           | 0.11    | 7.85% | 0.11     | 8612          | 190.06  | 2.21% | 500      | 0.27        | 0.89        | 4872        | 175.45         | 201.05  |
| 10             | HYDROXYPROPAZINE| 4.42      | 0.10    | 2.28% | 0.10     | 8612          | 190.06  | 2.21% | 500      | 0.27        | 0.89        | 4872        | 175.45         | 201.05  |
| 11             | LINURON| 1.41           | 0.11    | 7.85% | 0.11     | 8612          | 190.06  | 2.21% | 500      | 0.27        | 0.89        | 4872        | 175.45         | 201.05  |
| 12             | HYDROXYPROPAZINE| 5.74      | 0.11    | 18.8% | 0.11     | 136158       | 2095.95 | 1.54% | 500      | 0.08        | 0.25        | 110923      | 2802.78        | 201.05  |
| 13             | ALACHLOR| 0.37           | 0.03    | 9.03% | 0.03     | 128           | 19.25   | 15.00%| 500      | 7.15        | 23.85       | 30          | 7.60          | 201.05  |

Where: mean peak area n = 8

Column heading - MDL signal = mean peak area response

Column heading - MDL ugl⁻¹ = MDL concentration

Column heading - ugl⁻¹ = actual reportable concentration

Source water (Tab106 Table 5.12) was used to determine <MDL. Chosen due to its location and geographic similarity to River Ogmore
Table 5.18  River Ogmore water samples showing mean peak area response and MDL and reportable concentration for each compound

| Analyte number | Analyte                 | Mean Peak Area | Std Dev | % RSD | % of MDL (µg l⁻¹) | Mean Peak Area | Std Dev | % RSD | % of MDL (µg l⁻¹) | Mean Peak Area |
|----------------|-------------------------|----------------|---------|-------|-------------------|----------------|---------|-------|-------------------|----------------|
| 1              | ATRAZINE                | 160.2          | 34.30   | 21.40%| 2.55%             | 129.6          | 25.47   | 19.66%| 2.06%             | 0.86           |
| 2              | PROPAZINE               | 79.9           | 11.40   | 14.28%| 1.19%             | 57.1           | 25.28   | 44.27%| 0.85%             | 2.22           |
| 3              | ISOPROTURON             | 18.4           | 16.62   | 90.23%| 2.79%             | 22.7           | 14.84   | 65.51%| 3.43%             | 0.79           |
| 4              | DIURON                  | 1.2            | 0.97    | 40.57%| 0.41%             | 3.6            | 2.07    | 58.20%| 1.23%             | 0.41           |
| 5              | ATR-DESISOPROPYL        | 33.8           | 22.88   | 67.61%| 23.73%            | 77.1           | 45.01   | 58.36%| 14.79%            | 47.3           |
| 6              | ATR-DESETHYL            | 134.4          | 75.85   | 56.44%| 10.17%            | 133.3          | 83.96   | 62.96%| 10.10%            | 3.17           |
| 7              | SIMAZINE                | 19.9           | 5.56    | 27.89%| 1.47%             | 14.9           | 5.74    | 38.50%| 1.10%             | 0.39           |
| 8              | CYANAZINE               | 7.4            | 3.08    | 41.46%| 1.50%             | 4.1            | 1.78    | 43.22%| 0.83%             | 0.35           |
| 9              | ALACHLOR                | 2.5            | 1.81    | 73.14%| 0.59%             | 1.5            | 1.39    | 92.06%| 0.36%             | 0.11           |
| 10             | CHLORTOLURON            | 15.2           | 5.74    | 37.61%| 1.48%             | 12.4           | 3.57    | 78.99%| 1.30%             | 0.33           |
| 11             | LINURON                 | 2.6            | 1.40    | 57.85%| 0.92%             | 2.6            | 1.82    | 90.02%| 0.51%             | 0.50           |
| 12             | HYDROXYPROPAZINE        | 133.7          | 14.72   | 11.01%| 4.36%             | 40.3           | 16.48   | 40.86%| 1.32%             | 0.41           |
| 13             | ISOPROTURON_d6          | 22941          | 621.67  | 2.71% | 500               | 28611          | 540.19  | 1.89% | 500               | 26701          |
| 14             | SIMAZINE_d10            | 45089          | 1207.22 | 2.68% | 500               | 54096          | 1020.48 | 1.89% | 500               | 47558          |
| 15             | DIURON_d6               | 486            | 26.77   | 5.51% | 500               | 901            | 70.32   | 7.81% | 500               | 938            |
| 16             | ATRAZINE_d5             | 157815         | 3333.12 | 2.11% | 500               | 159669         | 2494.79 | 1.56% | 500               | 161801         |
| 17             | DIURON_d6               | 9753           | 332.65  | 3.41% | 500               | 9505           | 329.55  | 3.47% | 500               | 9542           |
Table 5.19  River Ogmore water samples showing mean peak area response and MDL and reportable concentration for each compound

| Analyte number | Analyte       | New Mill (14 July) | TAB156 unspiked | TAB157 unspiked | TAB158 unspiked |
|----------------|---------------|--------------------|-----------------|-----------------|-----------------|
|                |               | Mean Peak Area | Std Dev | % RSD | % of MDL (µg l⁻¹) | Mean Peak Area | Std Dev | % RSD | % of MDL (µg l⁻¹) | Mean Peak Area | Std Dev | % RSD | % of MDL (µg l⁻¹) |
| 1              | ATRAZINE      | 125.6             | 41.13   | 32.75% | 2.00% | 0.67 | 95.3 | 39.52 | 41.47% | 1.52% | 0.51 | 84.4 | 20.92 | 24.79% | 1.34% | 0.45 |
| 2              | PROPZINE      | 28.2              | 12.90   | 45.77% | 0.42% | 0.11 | 26.6 | 16.49 | 62.03% | 0.40% | 0.10 | 12.4 | 8.72  | 70.25% | 0.18% | 0.05 |
| 3              | ISOPROTURON   | 21.0              | 26.04   | 123.81%| 3.18% | 0.73 | 23.4 | 16.00 | 68.26% | 3.55% | 0.82 | 12.4 | 16.16 | 130.72%| 1.87% | 0.43 |
| 4              | DIURON        | 1.9               | 1.71    | 89.97% | 0.66% | 0.22 | 1.4  | 1.18  | 84.62% | 0.48% | 0.16 | 2.1  | 1.24  | 59.29% | 0.72% | 0.24 |
| 5              | ATR-DESISOPROPYL | 47.7            | 19.73   | 41.40% | 33.41%| 9.14 | 38.1 | 30.30 | 79.43% | 26.75%| 7.32 | 58.5 | 35.82 | 61.25% | 41.00%| 11.22 |
| 6              | ATR-DESETHYL  | 108.9             | 45.16   | 41.46% | 8.25% | 2.59 | 63.0 | 38.05 | 60.41% | 4.77% | 1.50 | 91.2 | 21.55 | 23.62% | 6.91% | 2.17 |
| 7              | SIMAZINE      | 11.8              | 6.10    | 51.86% | 0.87% | 0.31 | 9.9  | 3.56  | 36.00% | 0.73% | 0.26 | 8.0  | 2.99  | 37.49% | 0.59% | 0.21 |
| 8              | CYANAZINE     | 2.2               | 1.17    | 54.23% | 0.44% | 0.18 | 2.4  | 0.96  | 40.75% | 0.48% | 0.20 | 1.9  | 1.83  | 94.68% | 0.39% | 0.16 |
| 9              | ALACHLOR      | 2.0               | 2.62    | 134.37%| 0.47% | 0.14 | 1.7  | 1.92  | 115.70%| 0.40% | 0.12 | 2.7  | 2.79  | 101.78%| 0.66% | 0.19 |
| 10             | CHLORTOLURON  | 8.1               | 6.00    | 73.95% | 0.79% | 0.20 | 12.3 | 2.71  | 22.11% | 1.19% | 0.31 | 12.2 | 7.44  | 61.01% | 1.19% | 0.30 |
| 11             | LINURON       | 1.8               | 1.61    | 91.82% | 1.02% | 0.34 | 3.3  | 2.99  | 91.59% | 1.90% | 0.63 | 2.0  | 1.86  | 95.16% | 1.15% | 0.38 |
| 13             | HYDROXYPROPAZINE | 26.2            | 13.91   | 53.17% | 0.85% | 0.27 | 31.9 | 9.66  | 30.28% | 1.04% | 0.32 | 27.0 | 12.86 | 47.58% | 0.88% | 0.28 |

| Set 1          |               |                    |                  |                  |                  |
|----------------|---------------|--------------------|-----------------|-----------------|-----------------|
| 14             | ISOPROTURON d6| 21882              | 8849.15         | 40.44% | 500 | 17327 | 6765.84 | 39.05% | 500 | 20608 | 455.27 | 2.21% | 500 |
| 16             | SIMAZINE d10  | 48143              | 1461.22         | 3.04%  | 500 | 37636 | 2411.92 | 6.41%  | 500 | 34006 | 1402.08 | 4.12% | 500 |
| 17             | ALACHLOR d13  | 738                | 41.54           | 5.63%  | 500 | 403   | 62.27  | 15.46% | 500 | 287   | 29.94  | 10.43% | 500 |

| Set 2          |               |                    |                  |                  |                  |
|----------------|---------------|--------------------|-----------------|-----------------|-----------------|
| 12             | ATRAZINE d5   | 152332             | 4650.77         | 3.05%  | 500 | 152054| 3136.30 | 2.06%  | 500 | 165495| 39279.54 | 23.73% | 500 |
| 15             | DIURON d6     | 7444               | 3010.42         | 40.44% | 500 | 6909  | 2536.01 | 36.70% | 500 | 7095  | 406.69  | 5.73%  | 500 |

Where: mean peak area n = 8
Column heading - MDL signal = mean peak area signal response
Column heading - MDL µg l⁻¹ = MDL concentration in µg l⁻¹
Column heading - % of MDL = % of MDL concentration
Source water (Tab106 Table 5.12) was used to determine %MDL chosen due to its location and geographic similarity to River Ogmore
Table 5.20  River Ogmore water samples showing mean peak area response and MDL and reportable concentration for each compound

| Analyte number | Analyte          | Mean Peak Area | Std Dev | % RSD | % of MDL | Mean Peak Area | Std Dev | % RSD | % of MDL | Mean Peak Area | Std Dev | % RSD | % of MDL |
|----------------|------------------|----------------|---------|-------|----------|----------------|---------|-------|----------|----------------|---------|-------|----------|
| 1              | ATRAZINE         | 332.6          | 29.65   | 8.92% | 5.30%    | 298.4          | 28.04   | 9.40% | 4.75%    | 277.6          | 32.59   | 11.74%| 4.42%    |
| 2              | PROPZINE         | 25.8           | 14.65   | 56.66%| 0.38%    | 17.0           | 7.92    | 46.64%| 0.25%    | 7.6            | 6.49    | 85.21%| 0.11%    |
| 3              | ISOPROTURON      | 10.4           | 11.70   | 112.49%| 1.57%    | 9.6            | 4.23    | 44.23%| 1.45%    | 25.1           | 46.82   | 186.76%| 3.79%    |
| 4              | DIURON           | 5.3            | 6.17    | 116.82%| 1.83%    | 4.4            | 2.56    | 57.64%| 1.54%    | 5.6            | 6.13    | 109.64%| 1.93%    |
| 5              | ATR-DESISOPROPYL | 13.4           | 18.68   | 139.36%| 9.40%    | 19.1           | 16.53   | 86.69%| 13.37%   | 81.4           | 99.70   | 122.46%| 57.08%   |
| 6              | ATR-DESETHYL     | 303.2          | 44.89   | 14.81%| 22.96%   | 327.0          | 96.05   | 29.37%| 24.76%   | 256.7          | 28.16   | 10.97%| 19.43%   |
| 7              | SIMAZINE         | 50.9           | 10.00   | 19.64%| 3.76%    | 46.0           | 9.46    | 20.56%| 3.40%    | 38.1           | 8.14    | 21.39%| 2.81%    |
| 8              | CYANAZINE        | 1.9            | 1.96    | 103.70%| 0.38%    | 1.9            | 2.12    | 110.69%| 0.39%    | 1.9            | 2.50    | 129.17%| 0.39%    |
| 9              | ALACHLOR         | 3.4            | 3.25    | 95.07%| 0.82%    | 2.7            | 2.69    | 101.32%| 0.64%    | 2.9            | 1.79    | 61.90%| 0.69%    |
| 10             | CHLORTOLURON     | 9.3            | 3.40    | 36.71%| 0.90%    | 13.2           | 4.04    | 30.56%| 1.28%    | 11.3           | 6.08    | 53.98%| 1.10%    |
| 11             | LINURON          | 1.6            | 1.84    | 114.07%| 0.94%    | 2.5            | 2.08    | 82.53%| 1.47%    | 50.7           | 12.80   | 25.25%| 1.65%    |
| 12             | HYDROXYPROPAZINE | 55.5           | 32.24   | 58.07%| 1.81%    | 45.1           | 19.13   | 42.45%| 1.47%    | 50.7           | 12.80   | 25.25%| 1.65%    |

Where: mean peak area n = 8
Column heading - MDL signal = mean peak area signal response
Column heading - MDL ug l⁻¹ = MDL concentration in µg l⁻¹
Column heading - ug l⁻¹ = actual reportable concentrations

Source water (Tab106 Table 5.12) was used to determine %MDL chosen due to its location and geographic similarity to River Ogmore
Source water (Tab106 Table 5.12) was used to determine %MDL chosen due to its location and geographic similarity to River Ogmore.
Figure 5.17 River Ogmore, analyte concentration of the 12 compounds studied expressed as a percentage of the MDL of each compound

Compounds 1 to 13 are identified in Table 5.21 (analyte number)
## Table 5.22  River Ely water samples showing mean peak area response and MDL and reportable concentration for each compound

| Analyte Number | Analyte | TAB115 unspiked | TAB16 unspiked | TAB120 unspiked | TAB121 unspiked |
|----------------|---------|-----------------|----------------|----------------|----------------|
|                |         | Mean Peak Area  | Std Dev | % RSD | % MDL (µg l⁻¹) | Mean Peak Area | Std Dev | % RSD | % MDL (µg l⁻¹) | Mean Peak Area | Std Dev | % RSD | % MDL (µg l⁻¹) | Mean Peak Area | Std Dev | % RSD | % MDL (µg l⁻¹) |
| 1              | ATRAZINE| 98              | 18.10    | 18.37%| 1.57% | 0.53 | 64 | 18.81 | 29.23%| 3.03% | 0.34 | 72 | 41.00 | 57.09%| 1.14% | 0.38 | 88 | 43.03 | 46.74%| 1.41% | 0.47 |
| 2              | PROPAZINE| 30             | 29.45    | 98.49%| 0.45% | 0.11 | 6  | 4.13  | 74.80%| 0.08% | 0.02 | 11 | 9.75  | 89.11%| 0.16% | 0.04 | 15 | 22.35 | 153.65%| 0.22% | 0.06 |
| 3              | ISOPROPROTURON| 24           | 22.90    | 93.97%| 2.67% | 0.95 | 14 | 7.02  | 55.70%| 2.04% | 0.47 | 18 | 21.05 | 116.17%| 2.71% | 0.64 | 21 | 13.66 | 49.83%| 4.15% | 0.96 |
| 4              | DIURON  | 3               | 4.19     | 124.66%| 1.16% | 0.39 | 2  | 1.24  | 56.19%| 0.77% | 0.26 | 3  | 2.85  | 81.38%| 1.21% | 0.40 | 1  | 0.98  | 74.81%| 0.45% | 0.15 |
| 5              | ATR-DESISOPROPYL| 16           | 11.06    | 68.54%| 11.31%| 3.10 | 2  | 1.13  | 52.41%| 1.51% | 0.41 | 8  | 6.10  | 72.12%| 5.86% | 1.60 | 6   | 3.02  | 46.08%| 4.40% | 1.21 |
| 6              | ATR-DESETHYL| 79             | 32.43    | 41.30%| 5.95% | 1.87 | 95 | 71.81 | 75.94%| 7.16% | 2.25 | 108 | 23.52 | 22.17%| 8.17% | 2.56 | 122 | 24.34 | 19.91%| 9.23% | 2.90 |
| 7              | SIMAZINE| 14              | 7.85     | 51.03%| 1.02% | 0.36 | 10 | 4.81  | 46.93%| 0.76% | 0.27 | 11 | 7.62  | 87.88%| 0.33% | 0.29 | 10  | 8.85  | 92.70%| 0.71% | 0.25 |
| 8              | CYANAZINE| 1               | 1.25    | 100.97%| 0.25% | 0.10 | 1  | 1.26  | 137.48%| 0.19% | 0.08 | 2  | 2.15  | 135.01%| 0.32% | 0.14 | 2   | 2.69  | 119.34%| 0.35% | 0.15 |
| 9              | ALACHLOR| 4                | 3.18    | 76.78%| 0.98% | 0.29 | 3  | 5.14  | 152.55%| 0.81% | 0.24 | 3  | 4.29  | 125.00%| 0.82% | 0.24 | 2   | 1.51  | 81.85%| 0.44% | 0.13 |
| 10             | CHLOROXYLURON| 8             | 4.33    | 59.30%| 0.76% | 0.20 | 8  | 2.80  | 37.04%| 0.73% | 0.19 | 17 | 4.19  | 25.26%| 1.61% | 0.41 | 17  | 6.57  | 39.01%| 1.68% | 0.43 |
| 11             | LINURON | 2               | 1.68    | 100.96%| 0.97% | 0.32 | 3  | 4.98  | 150.83%| 1.92% | 0.64 | 3  | 2.91  | 77.14%| 1.51% | 0.50 | 2   | 1.20  | 52.76%| 1.33% | 0.44 |
| 12             | HYDROXYPROPAZINE| 41           | 15.62    | 38.56%| 1.34% | 0.42 | 29 | 12.84 | 43.99%| 0.95% | 0.30 | 74 | 16.03 | 21.67%| 2.41% | 0.75 | 69  | 28.53 | 41.57%| 2.24% | 0.70 |
| 13             | ATRAZINE (unspiked) | 2635       | 6666.27  | 25.03%| 0.50  | 0.22 | 500 | 16062 | 364.80 | 2.27% | 500 | 10331 | 2755.29 | 26.67%| 500 | 10926 | 657.70 | 6.02% | 500 |
| 14             | SIMAZINE _010| 32517      | 9757.41  | 30.01%| 0.50  | 0.22 | 500 | 31551 | 1986.45 | 6.30% | 500 | 33663 | 900.21 | 2.67% | 500 | 39963 | 3156.77 | 7.95% | 500 |
| 15             | CHLOROXYLURON| 1342       | 56.61    | 2.92% | 0.50  | 0.22 | 500 | 523   | 60.17 | 11.50%| 500 | 181   | 24.19 | 13.33%| 500 | 250   | 25.56 | 10.24%| 500 |
| 16             | DIURON  | 36              | 143577   | 4144.42| 2.89%| 0.50 | 14461 | 2347.88 | 1.98%| 500 | 144027 | 6169.63 | 4.28%| 500 | 121754 | 43249.34 | 25.73%| 500 |
| 17             | ALACHLOR| 3714           | 1198.34  | 32.36%| 0.50  | 4760 | 416.15 | 8.71% | 0.50  | 6962 | 212.60 | 3.05% | 500 | 7521 | 324.90 | 4.32% | 500 |

Where: mean peak area n = 8
- Column heading - MDL signal = mean peak area signal response
- Column heading - MDL µg l⁻¹ = MDL concentration in µg l⁻¹
- Column heading - µg l⁻¹ = actual reportable concentrations

Source water (Tab106 Table 5.12) was used to determine %MDL chosen due to its location and geographic similarity to River Ely.
Table 5.23  River Ely water samples showing mean peak area response and MDL and reportable concentration for each compound

| ELY | St. Georges (8 May) | Llancaervern (8 May) |
|-----|---------------------|----------------------|
| See Column Headings | TAB122 unspiked | TAB123 unspiked | TAB117 unspiked |
| Analyte number | ATRAZINE | Mean Peak Area | Std Dev | % RSD | % of MDL (µg l⁻¹) | Mean Peak Area | Std Dev | % RSD | % of MDL (µg l⁻¹) | Mean Peak Area | Std Dev | % RSD | % of MDL (µg l⁻¹) |
| 1 | ATRAZINE | 82 | 33.20 | 40.26% | 4.41% | 0.44 | 72 | 22.98 | 32.10% | 1.14% | 0.38 | 58 | 29.82 | 50.99% | 0.93% | 0.31 |
| 2 | PROPZINE | 10 | 13.90 | 135.45% | 0.15% | 0.04 | 23 | 52.47 | 231.34% | 0.34% | 0.09 | 22 | 21.26 | 97.74% | 0.32% | 0.08 |
| 3 | ISOPROTURON | 34 | 37.36 | 108.62% | 5.20% | 1.20 | 10 | 6.35 | 61.61% | 1.56% | 0.36 | 7 | 5.01 | 72.29% | 1.05% | 0.24 |
| 4 | DIURON | 3 | 5.77 | 176.83% | 1.13% | 0.38 | 5 | 6.41 | 126.51% | 1.75% | 0.59 | 3 | 2.96 | 118.45% | 0.86% | 0.29 |
| 5 | ATR-DEISOPROPYL | 6 | 5.86 | 93.50% | 4.39% | 1.20 | 9 | 7.44 | 80.92% | 6.44% | 1.76 | 48 | 15.01 | 31.55% | 33.36% | 9.13 |
| 6 | ATR-DEETHYL | 144 | 58.29 | 40.57% | 10.88% | 3.41 | 129 | 38.34 | 29.73% | 9.76% | 3.07 | 68 | 51.20 | 75.71% | 5.12% | 1.61 |
| 7 | SIMAZINE | 11 | 8.39 | 73.49% | 0.84% | 0.30 | 11 | 8.03 | 75.25% | 0.79% | 0.28 | 13 | 5.99 | 47.05% | 0.94% | 0.33 |
| 8 | CYANAZINE | 2 | 2.25 | 130.32% | 0.35% | 0.15 | 2 | 0.95 | 59.98% | 0.32% | 0.13 | 19 | 9.32 | 48.87% | 3.86% | 1.62 |
| 9 | ALACHLOR | 3 | 2.19 | 85.00% | 0.62% | 0.18 | 2 | 3.19 | 135.18% | 0.57% | 0.17 | 3 | 4.34 | 129.68% | 0.80% | 0.24 |
| 10 | CHLORTOLURON | 5 | 2.23 | 42.50% | 0.51% | 0.13 | 6 | 3.40 | 60.76% | 0.54% | 0.14 | 8 | 2.99 | 37.91% | 0.77% | 0.20 |
| 11 | LINURON | 2 | 2.43 | 118.22% | 1.20% | 0.40 | 2 | 1.03 | 43.38% | 1.38% | 0.46 | 3 | 2.37 | 75.52% | 1.85% | 0.61 |
| 12 | HYDROXYPROPAZINE | 49 | 18.59 | 37.74% | 1.61% | 0.50 | 58 | 14.93 | 25.78% | 1.89% | 0.59 | 48 | 21.19 | 43.96% | 1.57% | 0.49 |
| 13 | ISOPROTURON d6 | 6465 | 120.74 | 1.87% | 1.78% | 0.50 | 10036 | 141.42 | 1.41% | 0.00% | 500 | 9976 | 1149.75 | 11.53% | 0.00% | 500 |
| 14 | SIMAZINE d10 | 34352 | 1516.50 | 4.41% | 2.46% | 0.50 | 36041 | 1339.07 | 3.72% | 0.00% | 500 | 34701 | 2245.50 | 6.47% | 0.00% | 500 |
| 15 | ALACHLOR d13 | 116 | 39.01 | 33.56% | 2.31% | 0.50 | 151 | 28.21 | 18.73% | 0.00% | 500 | 176 | 55.97 | 31.84% | 0.00% | 500 |
| 16 | ISOPROTURON d6 | 7457 | 522.34 | 4.32% | 2.28% | 0.50 | 7469 | 380.83 | 5.10% | 0.00% | 500 | 5569 | 1321.97 | 23.74% | 0.00% | 500 |

Where: mean peak area n = 8
Column heading - MDL signal = mean peak area signal response
Column heading - MDL ug.l⁻¹ = MDL concentration in µg l⁻¹
Column heading - ug.l⁻¹ = actual reportable concentrations

Source water (Tab106 Table 5.12) was used to determine %MDL chosen due to its location and geographic similarity to River Ely
Figure 5.18 River Ely analyte concentration of the 12 compounds studied expressed as a percentage of the MDL of each compound

Compounds 1 to 13 are identified in Table 5.23 (analyte number)
5.8.1 Summary of Results.

This investigation determined 12 priority pesticides in three rivers in the South Wales area, the Wye, Ogmore and Ely using filtering and pre / post SPE extraction. The results indicate that the concentrations of the compounds under investigation were below the method detection limit of the instrument for each of the rivers sampled.

**River Wye:** The river was sampled on three separate days in 2009, on 8\textsuperscript{th} May, 14\textsuperscript{th} and 15\textsuperscript{th} July. Each sample was analysed for the 12 analytes listed in Tables 5.12 to 5.16 and in each sample the concentration of every compound was well below the method detection limit (MDL) of the instrument. For example taking atrazine from Table 5.12, shows the peak area response for a sample must be above the MDL signal threshold of 6277 and from the results of sample Tab 107 from Newbridge-on-Wye the mean peak area response was 126. This means the signal was below reportable limits and indicate a very low concentration of atrazine. The MDL signal for each analyte was different ranging from 6716 for propazine, to 143 for atrazine desisopropyl, the average signal was 1828.

Whilst the results are below reportable limits there is a trend in the concentrations of the analytes taken on different days and at different locations. Figure 5.16 shows the peak area analyte response against the % MDL for each sample and each compound for the River Wye. The results indicates all compounds are below 10% of the MDL except for atrazine desisopropyl which shows that 8 of 13 samples are above the 10% limit, the highest being 30.4%. Since atrazine desisopropyl is a metabolite of possibly four of the other compounds under investigation, namely atrazine, propazine, simazine and cyanazine, the atrazine desisopropyl signal may be higher because it might have more than one parent source but could indicate one or more parent compounds may have been present in the environment.
**River Ogmore:** The results outlined in Tables 5.18 to 5.21 also indicate the concentration of all 12 analytes under investigation fall below the analyte MDL each of the sampling locations. Figure 5.17 shows the peak area response against % MDL for all 12 compounds and as with the River Wye results, atrazine desisopropyl shows a higher response than any other analyte. The response against %MDL for 13 of the 14 results is greater than 10% and for 7 of the 14 it is greater than 30% with the highest being 57%. The other metabolite atrazine desethyl also shows an increased peak area response against %MDL with 11 out of 14 samples above 10% with the highest is being 22.9%

**River Ely:** The results (Tables 5.22 – 5.23) show a similar pattern to the other two rivers and that the MDL for each analyte under investigation falls below the reporting level for each compound. The peak area response against %MDL for the two metabolites, atrazine desisopropyl and atrazine desethyl are again higher than the other compounds (Figure 5.18) although the increase is a less than in other rivers. Only three of the metabolite samples were above 10 % but one of these was at 35%. All the other compounds in the River Ely study were below 5% of the %MDL.

### 5.9 Conclusions

This section has shown that the optimised sample preparation and analysis procedures discussed in previous chapters are fit for purpose and capable of the simultaneous detection of the widely differing target priority pesticide analytes.

The instrument limits of detection and limits of quantitation values calculated for spiked real river water samples show that the optimised methods, while not being specifically designed
to achieve the lowest detection limits, are capable of delivering results down at the level of the European drinking water directive.

This investigation of the priority pesticides in the Rivers Wye, Ely, Ogmore and Taff show that some of the metabolites concentrations measured approach but do not exceed the FDA MDL limit and none of the sampling points were above the MDL limit regardless if whether the rivers passed through agricultural, industrial or semi-rural areas.

In future, efforts should concentrate on narrowing the difference between the excellent instrumental LOD values and the MDL by reducing inter-replicate variation.
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