CATCHMENT MONITORING AND MANAGEMENT SYSTEMS – THE CHALLENGES FOR A PROJECT LABORATORY

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ABSTRACT:

The water quality monitoring requirements of a Catchment Monitoring and Management System present challenges for the project laboratory in terms of data quality and quantity. The projects require a high volume of quality controlled data to be generated and reported on in a short time span. This paper outlines the experience of the Boyne & Liffey Catchment Laboratory in the Three Rivers Project to show some of these challenges and the systems required to meet them. The laboratory analyses 8000 samples per year for a range of parameters including nutrients MRP, TON and Total P. The system of method verification and routine Analytical Quality Control is described. Issues critical to the achievement of a successful analytical programme include laboratory organisation, staffing and equipment. River water quality data from a forested upland catchment is presented to highlight the need to achieve low Limits of Detection. Data from the Liffey main channel is presented to show the importance of acceptable Accuracy and Precision when comparing datasets. The project laboratory model can deliver high quality data with high sample throughput for use in CMMS in an efficient and cost effective way. It is important to recognise that the appropriate analytical techniques are required for the successful implementation of the monitoring and analytical programme.

Keywords : analytical programme, catchment monitoring, method verification, quality control.

INTRODUCTION

The national biological monitoring programme of the EPA has shown an overall decline in water quality since 1971, with eutrophication caused primarily by excessive inputs of phosphorus identified as the major threat to the quality of surface waters in Ireland. In 1997 the policy document entitled " Managing Irelands Rivers and Lakes A Catchment Based Strategy Against Eutrophication" [(1)] was issued, with the aim of reversing the deterioration in water quality through catchment scale programmes. The catchment monitoring and management systems set up with EU and exchequer funding include the Lough Derg and Lough Ree project on the Shannon, Lough Leane project in Co. Kerry and the Three Rivers Project covering the Boyne, Liffey and Suir. The implementation of the Water Framework Directive [(2)] will see the expansion of catchment scale projects as a means to manage, improve and protect water resources.

The monitoring effort within these programmes is only one of several elements which must be pursued in order to achieve the stated aims of improving and protecting waters. It is, however, a vital contribution : it informs the overall process, providing feedback on progress to date and facilitating an intelligent targeting of resources to priority areas.

The Boyne and Liffey Catchment Laboratory was established in Trim, Co. Meath to monitor physico-chemical parameters for the Three Rivers Project within the Boyne and Liffey catchments. This paper discusses the challenges for the project laboratory in terms of data quality and the systems required to meet them.

Project aims :

1. Establish integrated and sustainable management system for each catchment
2. Establish baseline water quality conditions
3. Identify and quantify pressures on water resource
4. Develop method for prioritising sub-catchments in order to focus resources
5. Measure effectiveness of implementation of management strategies

Function of a project laboratory :
To deliver a coordinated water quality monitoring programme with sufficient spatial and temporal resolution to support the project aims.

THIS MEANS

1. High frequency sampling and analysis where load estimates are required
2. Analytical capabilities which are fit for purpose in terms of data quality.
3. Providing data to the consultants on a scheduled basis in a suitable digital format.

In other words : Quality and Quantity demands.

METHODS

The laboratory staff were recruited to start in September / October 1999, Laboratory equipment was selected and purchased in Oct 1999, equipment was installed by end of Nov 1999, followed by 2 weeks method commissioning and verification.

The project monitoring network for these 2 catchments comprises 135 grab sample sites, 7 autosampler sites and 62 hydrometric sites. These sites are visited between 40 and 50 times per year resulting in a sample throughput of approx 8000 samples per year including Autosamples.

The parameters monitored are:
Ammonia, MRP, TON, NO2, DO, Temp., pH, Conductivity – at all sites
Total P, Total N, DRP – at selected sites.

The project employs 2 sampling technicians who take in-situ measurements, collect grab samples, read staff gauges and service the Autosamplers. These field staff sample Monday to Thursday, delivering samples to the laboratory at the end of each day, and use Friday for Autosampler maintenance and laboratory work. The samples are refrigerated overnight and analysed by Flow Injection Analyser for NH3, MRP, TON and NO2 the following day. Samples for Total P analysis are digested each day and analysed in a batch each Monday. Therefore the autoanalyser has to operate 5 days per week. This arrangement is key to achieving high sample throughput and requires that the analyser is operated and maintained effectively in order to reduce downtime to an absolute minimum.
The laboratory staff originally consisted of 1 chemist and 1 analytical technician. However a second analytical technician was recruited and trained on the autoanalyser. This allowed the laboratory to operate at full analysis capability throughout the year.

Method Verification and Quality Control:

The analytical techniques used by the laboratory to measure nutrients in freshwater are well established methods based on standard colorimetric reactions and detection by spectrophotometry. An automated system such as Flow Injection Analysis can deal with high sample numbers but also offers low limits of detection and good precision. During the initial method commissioning phase each nutrient analysis method was verified to confirm that the method, as operated by our laboratory, satisfied key performance characteristics.

1. Method Detection Limit, based on repeated analysis of low level standards over 3 days. [(3)]
2. Precision, based on % RSD of repeat analyses for a range of standard concs.
3. Linearity, based on degree of fit of the calibration equation over the working standard range.
4. Spike Recovery, based on analysis of real matrix samples before and after spiking with a known amount of analyte.
5. Digestion efficiency, based on analysis of P or N compounds, added to de-ionised water and to real matrix solutions, which require chemical conversion prior to detection.

Once it is confirmed that the method performance is satisfactory the routine analysis can begin and routine Analytical Quality Control procedures must be employed to ensure that the method stays in control. AQC checks in our nutrient analysis include :

1. Calibration fit criterion, $r > 0.9990$
2. Analysis of check solutions, at the start and finish of each run, made from certified standard stock solutions which are traceable to NIST. These solutions are sourced independently of the calibration materials and the results used in control charts.
3. Analysis of blanks, calibration standard and duplicate samples every 20 analyses.
4. Participation in Proficiency Testing schemes. EPA Intercal Scheme, Aquacheck scheme and Central Science Laboratory LEAP Scheme 5 times per year.

The Proficiency testing schemes are particularly important as they are an external 3rd party assessment of analytical performance.

RESULTS

Some examples of method verification data and QC data are given below.

Table. 1. – Method Detection Limits : Boyne & Liffey Catchment Laboratory

	Method Detection Limit and Practical Quantitation Limit for Lachat Quickchem 8000 *Data produced over 3 days of analysis*					
	NH3	**MRP**	**TON**	**NO2**	**Total P**	**Total N**
	mg N/L	mg P/L	mg N/L	mg N/L	mg P/L	mg N/L
std conc.	0.010	0.004	0.100	0.004	0.004	0.100
Rep 1	0.010873	0.004298	0.104632	0.004003	0.003891	0.08785
2	0.009171	0.004696	0.100461	0.003964	0.002706	0.09485
3	0.009968	0.004874	0.101480	0.003819	0.003121	0.10522
4	0.010802	0.004606	0.099603	0.004132	0.003641	0.08424
5	0.011434	0.004663	0.101992	0.004113	0.004055	0.11161
6	0.009968	0.004368	0.100979	0.004005	0.004527	0.10033
7	0.010401	0.004343	0.103744	0.003878	0.004524	0.11152
mean	0.010374	0.004550	0.101842	0.003988	0.00378	0.09937
StDev	0.000745	0.000217	0.001790	0.000114	0.00068393	0.01091361
MDL (3.14*StDev)	0.0023	0.0007	0.0056	0.0004	0.0021	0.0343
PQL (5*MDL)	0.012	0.003	0.028	0.002	0.011	0.171

Note : Method Detection Limit based on methodology in Standard Methods. The PQL estimated at 5*MDL is indicative of the level at which reliable quantitative measurements can be made.

Table. 2. – Spike Recoveries 4 Channel Spike Recoveries						
Date:	22-Nov-02					
Samples spiked by: K. Cunningham						
Analyst: F. Quigley						
Analyte		**Compound**	**Intermediate Stock**	**Conc.**	**Dilution**	**Spiking Soln.**
NH3		NH4Cl	19.095g/L	5000mgN/L	50/500ml	500mgN/L
MRP		KH2PO4	4.391g/L	1000mgP/L	50/500ml	100mgP/L
TON		KNO3			14.440g/500ml	4000mgN/L
NO2		NaNO2	4.9260g/L	1000mgN/L	50/500ml	100mbN/ L
** Add 100uL of Spiking Solution to 200ml sample = 1/2000 dilution of spike						
Spike Factor			x + 0.250	x + 0.050	x + 2.050	x + 0.050
Description	**Sample ID**	**Site ID**	**NH3**	**MRP**	**TON**	**NO2**
			mg N/L	mg P/L	mg N/L	mg N/L
Unspiked	02997221	RS9L01600	0.014	0.012	1.101	0.006
Unspiked	02997221	RS9L01600	0.014	0.012	1.093	0.006
Unspiked	02997221	RS9L01600	0.014	0.012	1.091	0.006
Mean			0.013969667	0.012081	1.094758	0.006355333
SD			0.000365423	0.000185	0.00528614	4.20634E-05
Spiked	02997221	RS9L01600	0.261	0.062	3.079	0.054
Spiked	02997221	RS9L01600	0.261	0.061	3.077	0.054
Spiked	02997221	RS9L01600	0.261	0.061	3.084	0.054
Mean			0.261295	0.0615897	3.079845667	0.053735333
SD			0.00020538	0.0003269	0.00363672	9.79609E-05
% Recovery			**99.0**	**99.2**	**97.9**	**95.4**

Note : Acceptable % Recovery for spiked samples is 90 – 110 %.

Table 3 Total P Digestion Efficiency

Date :	27/08/02								
Operator:	F. Quigley								
Compound	**Dilution**	**Conc.**	**Result**	**Result**	**Result**	**Mean**	**SD**	**%RSD**	**% Recovery**
		mg P/L	**Dig1**	**Dig2**	**Dig3**				
$(NaPO_3)_6$	3.2903g/L	1000							
	1/50	20.00							
	1/100	0.20	0.196	0.197	0.192	0.195	0.003	1.393	**97.6**
	2/100	0.40	0.386	0.388	0.381	0.385	0.003	0.896	**96.2**
	3/100	0.60	0.576	0.582	0.577	0.579	0.003	0.536	**96.4**
AMP	1.2631g/L	100							
	1/5	20.00							
	1/100	0.20	0.196	0.196	0.191	0.194	0.003	1.384	**97.3**
	2/100	0.40	0.377	0.380	0.375	0.377	0.002	0.653	**94.3**
	3/100	0.60	0.554	0.540	0.555	0.550	0.008	1.524	**91.6**
PO_4	200mg/L								
	2.5/1000	0.50	0.469	0.468	0.469	0.468	0.001	0.172	**93.7**

Note: The Total P method is calibrated over the range 0 – 0.200 mg P/L, which covers the majority of samples. Samples above this range are not re-digested after dilution, rather the digest is re-analysed after dilution, so the digestion process must provide satisfactory recoveries above 0.200 mg P/L

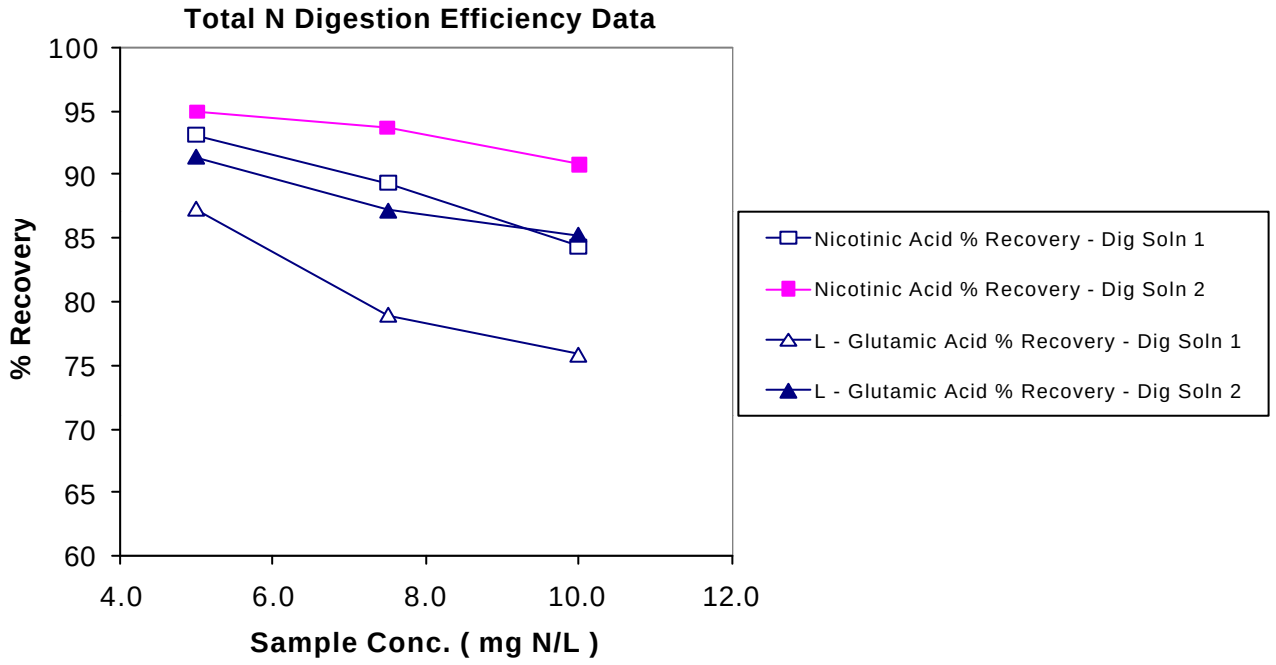

Fig. 1. – Total N Digestion Efficiency

The Total N method uses a Sodium Hydroxide, Potassium persulphate and Boric Acid digestion solution, with autoclaving. The initial method verification showed poor % Recoveries for L – Glutamic Acid. (Dig Soln 1). Tests were repeated using a digestion solution 3 times as concentrated, achieving satisfactory recoveries in the range of interest, up to 7.0 mg N/L (Dig Soln2).

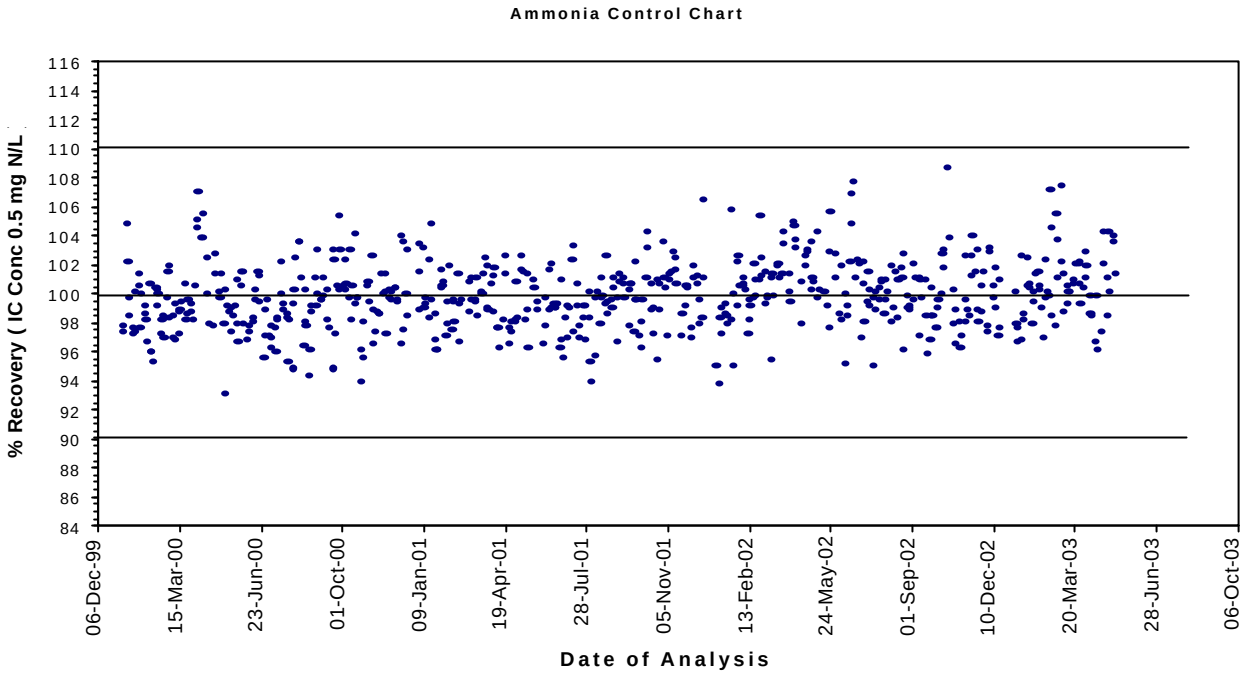

Fig. 2. – Control Chart for NH3 method.

Check Sample of 0.500 mg N/L is made from NIST traceable stock sourced independently of Calibration standards and analysed in every run.

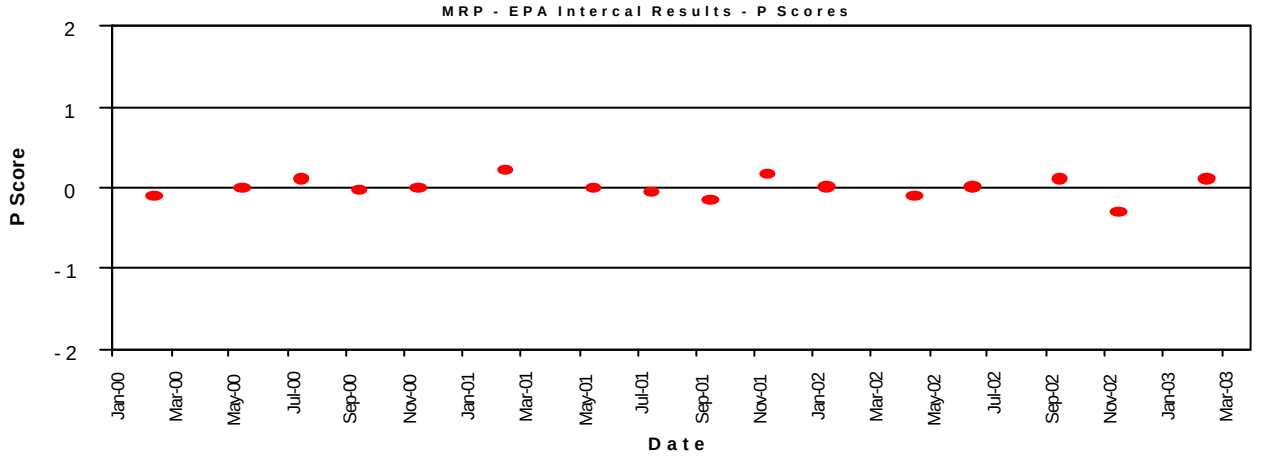

Fig. 3. – Results of EPA Intercalibration Scheme for MRP
P Score of 1 = 20% deviation from reference value.

By demonstrating satisfactory method performance and continued data quality through routine AQC the laboratory produces data with a total analytical error which is acceptably small. Included below are some cases showing the relevance of data quality issues in the context of river monitoring.

DISCUSSION

Case 1 :Kings Liffey Pilot Study Area, Upper Liffey Catchment, forested upland area.

This area was selected as a pilot study area with a view to ascertaining the effect of forestry operations on nutrient concentrations and loads. Although ambient P concentrations were typically very low (93% of all grab samples at downstream site < 0.010 mg P/L), the TP export coefficient calculated from flow proportional autosampling was 0.65 kg/ha/year, comparable to a low to medium intensity agricultural area [(4)] . This loading is accounted for by the high flow rates rather than high nutrient concentrations. Referring to the method verification data for MRP , the calculated MDL and PQL is 0.0007 and 0.0030 mg P/L respectively. From Figure 4 below it can be seen that reliable measurement of concentrations below 0.010 mg P/L is necessary to characterise water quality at this site.

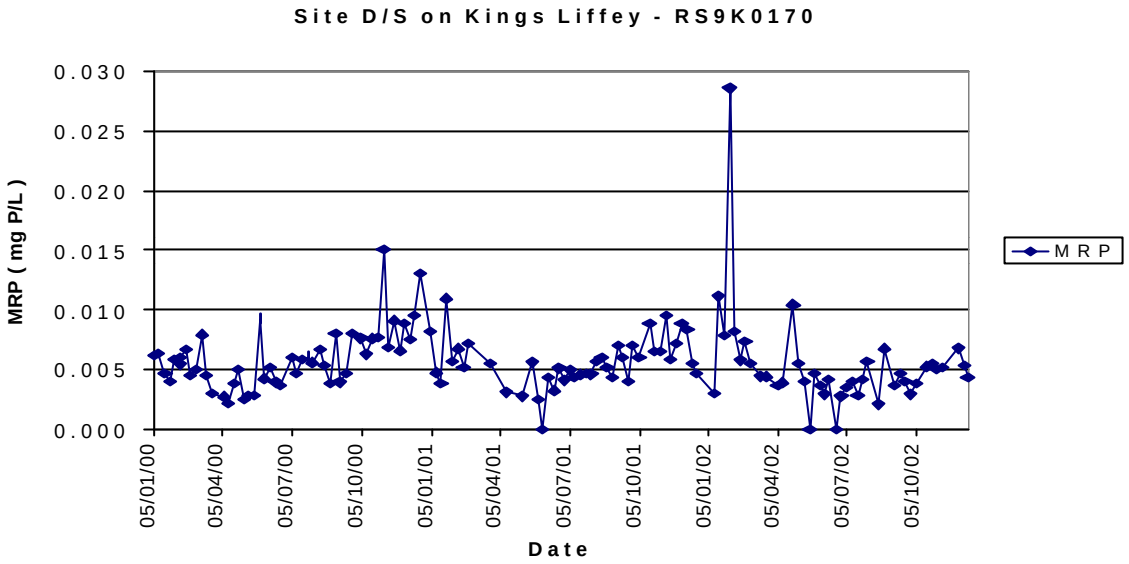

Fig 4. – MRP concentration on Kings Liffey, 2000 – 2002.

Case 2 : Comparing yearly datasets.

In the case of rivers, compliance with the 1998 Phosphorus Regulations [5] is assessed through the biotic Q values or annual median MRP concentrations, with improvements required by 2007. Annual medians are commonly used in assessing trends over time. Averages, such as median or mean, will overcome the effects of poor precision but systematic error or bias in the measurements is not removed by repeated measurement. This is particularly important when comparing data from different sources : is the apparent trend real or the result of the difference in bias between 2 laboratories? Interlaboratory Calibration schemes, spike recovery tests and routine QC such as analysis of blanks all contribute to the comparability of data in this case. Figure 5 shows annual median MRP along the main channel Liffey from 2000 to 2002. There has been a significant reduction in MRP concentrations as a result of the investment in MWWTPs at Osberstown and Leixlip. Note the close agreement of MRP values in the upstream section over the 3 years. Each annual median is based on approx 45 sampling events. (For a discussion of sampling frequencies required to show statistically significant trends given the high variance of data for some water quality parameters see the EPA document on the National Rivers Monitoring Programme, March 2002 [6] .)

CONCLUSIONS

The project laboratory model

1. Dedicated facility – clearly defined role, one primary function : provide data for project
2. Can afford to specialise – in terms of required equipment and suitable analytical methods
3. High level of operational competency built up quickly – autoanalyser run 5 days per week
4. Workload is constant, predictable – allows staff to plan and manage tasks
5. Staff – have experience in autoanalysers and competence to trace metals analysis standard, e.g acid soaking of glassware as in trace analysis is required for Total P digestions.
6. Centralised – can afford and put to use high throughput equipment
7. Training – sufficient staff trained to provide full analytical operation throughout the year.
8. Running costs of approximately € 30 per sample, excluding the cost of building rental and administrative support provided by Meath County Council.

Data quality and traceability

There is an increasing awareness of the importance of ensuring data quality and traceability in environmental monitoring. The Drinking Water Regulations, 2000 [7] set out data quality requirements in terms of the acceptable accuracy, precision and Limit of Detection for the various parameter tests. The operation of a laboratory quality assurance system recognised by accreditation to ISO/IEC 17025 [8] would address the full range of data quality requirements including measurement traceability and measurement uncertainty. Accreditation would be best pursued in the context of defined medium to long term arrangements where the planning and resource commitments could be met.

Performance

Finally, the model as outlined in the case of the Boyne & Liffey catchments has delivered a high level of performance and high sample throughput at relatively low cost, providing the catchment monitoring and management system with the high resolution data needed to inform and guide the management process.

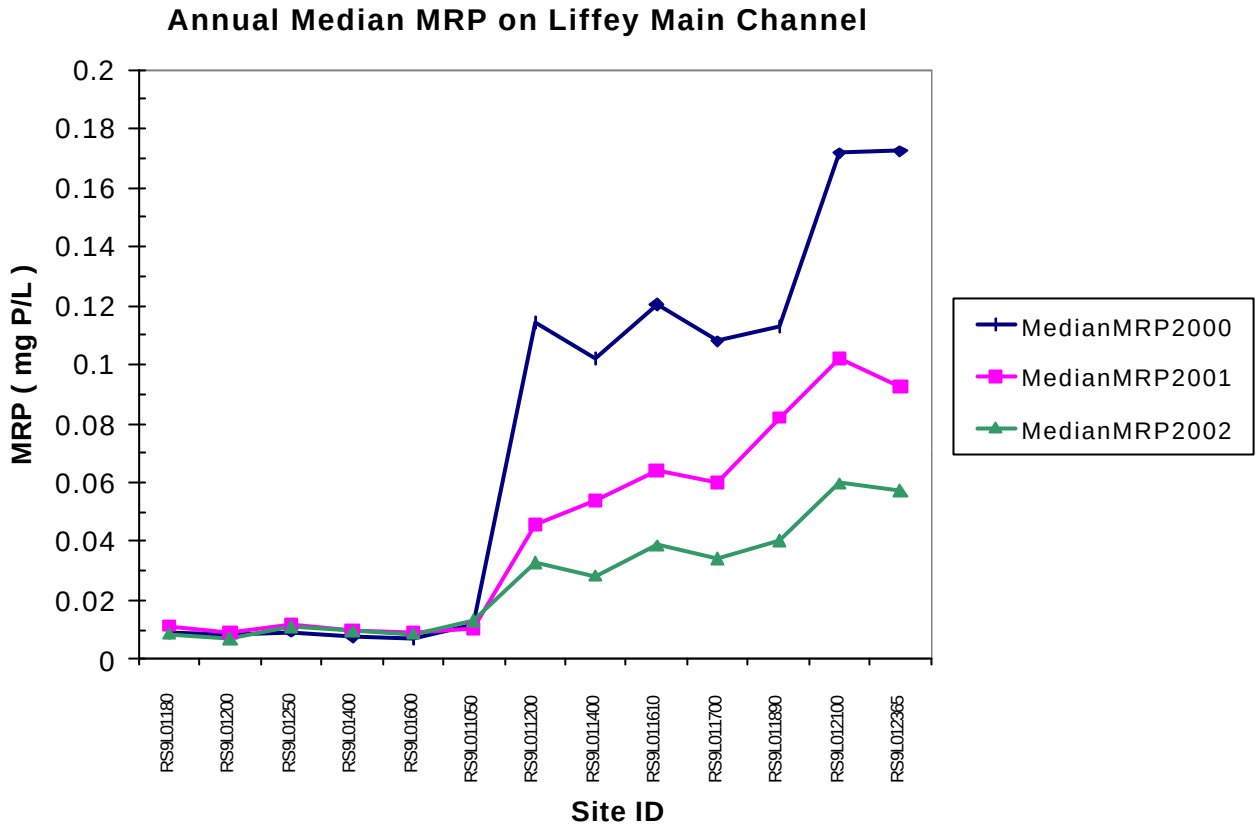

Fig. 5. – Annual median MRP along main channel Liffey over 3 years.

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REFERENCES

Managing Irelands Rivers and Lakes – A Catchment Based Strategy Against Eutrophication, Department of Environment and Local Government (1997)

Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.

Standard Methods for the Examination of Water and Wastewater, 20th edition, American Public Health Assoc., American Water Works Assoc., Water Environment Federation (1998).

Three Rivers Project Final Report, M.C. O'Sullivan & Co. Ltd (2002)

Local Government (Water Pollution) Act 1977 (Water Quality Standards for Phosphorus) Regulations, 1998. S.I. No. 258 of 1998

National Rivers Monitoring Programme (Incorporating Monitoring Requirements of the Water Framework Directive), E.P.A. (March 2002)

European Communities (Drinking Water) Regulations, 2000. S.I No. 439 of 2000.

ISO/IEC 17025:1999 General requirements for the competence of testing and calibration laboratories