Tales of the Riverbank

A problem solving case study in analytical chemistry and environmental science

THE UNIVERSITY OF HULL

RSC | Advancing the Chemical Sciences

UNIVERSITY OF PLYMOUTH

Tales of the Riverbank

A problem solving case study in analytical chemistry and environmental science

Devised by

Simon Belt
School of Environmental Sciences, University of Plymouth, Plymouth, PL4 8AA

Tina Overton
Department of Chemistry, University of Hull, Hull, HU6 7RX

Stephen Summerfield
Department of Chemistry, University of Hull, Hull, HU6 7RX

Preface

'Tales of the Riverbank' is one of six problem solving case studies that have been designed in order to teach analytical and applied chemistry within a 'real' life context by developing problem solving and professional skills.

Employers have long urged the Higher Education sector to produce graduates with a range of transferable skills that would make them more immediately effective in the world of work. To produce graduates who can operate in the workplace professionally, we need to go much further than just ensuring that they have a sound knowledge of chemistry, adequate practical abilities and rudimentary problem solving skills. We must ensure graduates can think critically and analytically, can interpret data and information, tackle unfamiliar open-ended problems and apply their chemical knowledge. In addition, the modern graduate must master a range of 'professional' or transferable skills including communication, team working, time management, information management, independent learning and the use of information technology.

Our approach in producing resources that address these issues in analytical chemistry has been to develop problem-solving case studies that use the contexts of forensic science, pharmaceuticals, environmental science, and industrial chemistry. These present extended problems are set in a 'real' context with incomplete or excessive data, and require independent learning, evaluation of data and information and, in some cases, do not lead to a single 'correct' answer. By tackling these cases, students are able to see the relevance of analytical chemistry and so approach the activities with enthusiasm and interest. The analytical skill developed throughout the case studies closely follow those recommended by the United Kingdom Analytical Partnership (UKAP). In addition, the transferable skills listed for each case study correlate with those identified in the RSC Undergraduate Skills Record documentation.

A Dip in the Dribble	Analytical, environmental and industrial chemistry
Launch-a-Lab	Industrial chemistry and advanced professional skills
New Drugs for Old	Pharmaceutical and analytical chemistry
Tales of the Riverbank	Analytical chemistry and environmental science
The Pale Horse	Analytical chemistry and forensic science
The Titan Project	Industrial and analytical chemistry

The case study has been extensively trialled, modified and updated. We feel that it is now in a suitable form for more widespread use. Whilst we have made every effort to ensure that this case study is free of errors and the guidelines for delivery are unambiguous, almost inevitably, we will have overlooked some detail. If users come across any errors or have any suggestions for further improvement we would be pleased to hear from you.

We thank the Royal Society of Chemistry Analytical Trust Fund for the funding of this project and the enthusiastic support of the United Kingdom Analytical Partnership (UKAP). We acknowledge Bob Knight and Tom McCreedy (University of Hull), Hugh Flowers (Glasgow University), Bob Mackison (Chemical Solutions), Jim Miller, Helen Reid and Barry Sharp (Loughborough University), Naaman Ostah, Chris Harrison and Graham Lawson (De Montford University) and Hywel Evans (University of Plymouth) for their invaluable feedback and encouragement. Finally, we are indebted to all the friends, students and staff at various universities who have helped in the development of these case studies by their enthusiastic participation.

For further details contact: -

Dr. Tina Overton, Department of Chemistry, The University of Hull, Hull, HU6 7RX, UK
Telephone (01482) 465453 E-mail t.l.overton@hull.ac.uk

Dr. Simon Belt, School of Environmental Sciences, University of Plymouth, Plymouth, PL4 8AA
Telephone (01752) 233042 E-mail sbelt@plymouth.ac.uk

Contents

Aims of the Case Study

This problem-based case study is set within the fictitious Coley River system in the county of Midshire. The environmental problems encountered in the river are organic, inorganic and physical in nature. This provides students with a ‘real’ context with which to extend their knowledge of analytical chemistry and to give them the experience of tackling an extended open-ended problem.

Students assume the role of the investigation team following a complaint about a reduction in the number and size of fish caught along a local river. By considering both temporal and spatial factors, the students identify an array of possible causes. As further data and information is made available, the groups are required to consider environmental issues, pollution, sampling, analytical techniques, water quality, data analysis / interpretation, toxicity, and remediation.

Who is the case study aimed at?

The case study works well with students at levels 2 and 3.

How long does the case study last?

The minimum contact time required is 5-6 hours and will require the students to spend approximately 12 hours in associated independent study.

How can the activities be assessed?

Various methods of assessment can be used including group or individual report, oral presentations, and contribution to group.

What are the learning outcomes?

They must apply appropriate knowledge of analytical techniques to tackle an extended and open-ended problem. The nature of the activities involved ensure that, in order to complete the case study, students must develop a variety of scientific (table 1) and transferable skills (table 2).

Table 1: Scientific skills

Disciplines covered	Analytical chemistry, environmental science, ecotoxicology,
Scientific knowledge	Selecting the appropriate analytical technique, sampling strategies, spectrophotometry, electrochemical testing (pH, conductivity, COD), GLC (organic pollutants), ICP (heavy metals), IC (anions) and environmental classification (river quality by chemical and biological indicators.)
Handling information	Manipulation and evaluation of information and data to make realistic decisions on the evidence available.
Problem Solving	Tackling unfamiliar problems, using judgement, evaluating information, formulating hypotheses, analytical and critical thinking.

Table 2: Transferable skills

Communicatio n skills	Oral presentations and report writing.
Improving learning and performance	Using feedback to reflect upon group and individual performance. Drawing on the experience within the group.
Information technology	Word processing reports and preparing material for presentations.
Planning and organisation	Individual judgement, decision making, analysis, time management, planning, prioritising and working to tight deadlines.
Working with others	Brainstorming, discussion, division of tasks and feeding back to the group.

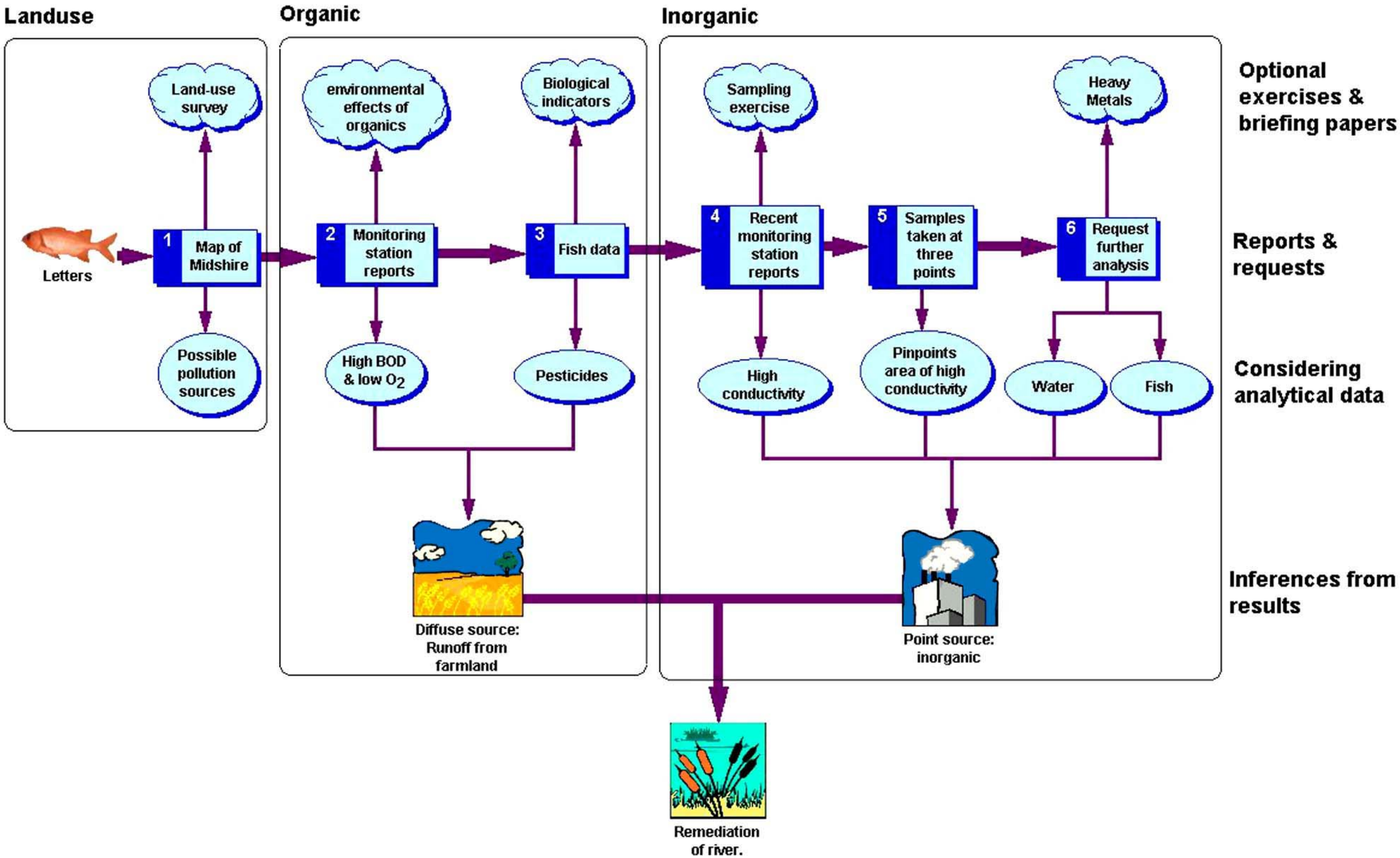


Figure 1: The case at a glance

Making it work

The class is divided into groups of 3-6 with four being the optimum number. It is advisable to randomise the groups so that each has a range of abilities and skills.

Initial correspondence

The case study can be introduced by giving out the letter from Arthur Pickles of the Beauport Angling Association who have observed a reduction in the number and size fish caught between Atwood and Coley Bridge. The students, acting on behalf of Midshire River Authority, investigate whether there is any credence to this complaint and, if so, what the possible the causes of the problem could be.

The River Coley arises from springs in limestone hills. The water in the upper reaches is clear. It is not until the tidal reach at Coley Weir that the water becomes turbid. Since the clean-up in the 1990s, lead by Midshire River Authority and Beauport County Council, the Coley River has once again become renowned for trout fishing.

The dumping of untreated industrial waste and sewage has been stopped with the building of treatment works at Gottland Water and Beauport. The industries and land use are simplified from the complexity that would be found along a real river system.

Landuse along the Coley River

Students survey the use of land along the Coley River and consider the industrial and agricultural inputs that could be potential polluters. This becomes especially important when considering the inorganic problem. This may be done by giving each group an overhead of the 'survey of land-use.' In the next session the groups feed back to the rest of the class.

Data from the monitoring stations.

Students are given historical data for the four monitoring stations along the River Coley over the last three years. They should be able to determine that there is a seasonal problem occurring during the winter months. The high BOD and ammonia with subsequent reduction in dissolved oxygen is indicative of organic pollution.

Request for Organic Analysis

Students can request further analysis from the four monitoring stations. Most students request the analysis of water even though they have realised that the problem is seasonal and it is out of season for the indicated problem. The levels are below the limit of detection.

The determination of organics in sediments would be too expensive and lengthy but an excellent method once the source has been identified.

Fish that live in the river all the year round are useful biological indicators. Their population is an excellent biological indicator. The analysis of their livers reveals an increase in the level of paraquat (a herbicide) of over an order of magnitude. This confirms that the pollution is probably runoff from Finley's agricultural farm but cannot be proved until winter, when the problem is likely to occur again.

Recent data from monitoring stations.

The students are given the recent data. This shows a large increase in conductivity between Coley Bridge and Atwood. So this further problem is inorganic in nature.

Sampling

The students are given a more detailed map and choose three sampling points. The number of sampling points permitted is limited to encourage critical thinking and avoid excessive number of requests being made. This focuses the students into thinking about where they should sample in order to narrow down where the pollution could be originating.

The students are given the biological oxygen demand (BOD), chemical oxygen demand (COD), conductivity, ammonia, dissolved oxygen and appearance for these three points.

Requests for further analysis

Students request further analysis to identify possible source(s) of the pollution. This also provides those students who did not choose suitable sampling points a second chance to identify that the inorganic pollution originates from a tributary of the Coley River.

Students make requests to the environmental laboratory on *'Analysis Request Forms'* (see Appendix A) and must specify clearly the analytical technique required.

Submitted requests are useful in charting the progress in the case and also flag up areas that the tutor needs to explain e.g., remind the students that NMR, MS and FT-IR cannot solve all their analytical problems.

When making requests, students should consider the following.

- What samples do they want analysed?
  The students should enter the sampling point and the type of sample (water, fish, sediment etc.)

- What analytical techniques are suitable?
  It should be stressed that the students should request the method of analysis that is most appropriate for the particular analyte.

- What levels can be detected by the method?
  If the method cannot detect a compound or element then this is expressed on 'Result Cards' in terms of 'less than' giving an indication of the limit of detection.

- What would normal concentrations be?
  This can be assessed by looking at areas of the river that have not been polluted (e.g. points 1 and 2).

Students should be encouraged to carry out any necessary independent study so that they make the best use of the limited number of requests. By making sensible requests, students should be able to identify the sources of the pollution.

Results Cards
Data for monitoring stations 1-4 are supplied to the students at the discretion of the tutor but provide the students with information on the normal levels in the river.

Blank *'Results Cards'* are provided for any other responses that have not been covered already. This also allows the tutor to assist the students however he/she chooses. For example, indicating why the results would not be useful and suggest another method of analysis.

The Report

The students are expected to submit a report to the Midshire River Authority. This should identify the probable cause(s) of the depletion in fish numbers, summarise their evidence, and decide what further evidence is required.

In addition, it should suggest how the problems could be avoided in the future, indicate what remediation would be performed and briefly describe how they would monitor whether they are having any effect.

Debriefing

It is recommended that at the conclusion of the case study, the tutor leads a debriefing session.

This is an opportunity to not only discuss the details of the case, but to enable students to evaluate the role of analytical science in solving this case, and help them reflect on their own development in terms of knowledge and skills.

Presentation and Assessment

Students may be assessed in different ways.

- **Exercises**
  The sampling, organic analysis and inorganic analysis exercises (Appendix C) are optional and can be used to focus the students on areas that may require detailed private study or that the tutor may want to highlight.

- **One page results summary**
  This may be useful for the tutor who can easily see what evidence the assumptions have been based upon without referring back to the evidence request forms.

- **Written report (group or individual)**

- **Group oral presentation**

- **Contribution to the Group**
  This can be used to judge individual student's contribution to the activity and is particularly useful in situations when a group has failed to work well.

Table 3: Examples assessment schemes

Group written report	50%
Group oral presentation	50%
	100%

Organic analysis (individual)	20%
Sampling exercise (individual)	20%
Inorganic analysis (individual)	20%
Group Report	30%
Group oral presentation	10%
	100%

Any Questions?

1. **Why is there no scale of the map?**
   It is not important.

2. **Where exactly are points 1 and 4?**
   Point 1 is on the eastern edge of the map upstream of Atwood
   Point 4 is between Beauport and the Water Treatment Plant

3. **Has the Angling Club increased in membership, changed the restocking policy or done anything to increase pressure on fish stocks?**
   The membership has shown a small increase. It has no control over restocking for the River Coley. There has been little change in the volume of fishing over the last 20 years.

4. **How far up the River Coley is it tidal?**
   At the Weir, just west of the Coley Bridge.

5. **Are there sewage treatment works at Atwood, Beauville and Montford?**
   Gottland Water is a drinking water treatment works. Beauport is the major sewage treatment works. Each small town has a secondary sewage treatment works that are discharging into the river.

6. **Which of the industries discharge effluents into the river and which into the sewer system?**
   All industries are point sources that discharge effluents into the river or sewer depending upon consent. The farms are disperse sources that discharge into the river.

7. **What were the weather and river levels like in July and August?**
   July and August were dry and so there was low river flow.

8. **What is the fertiliser referred to at Finley's Farm?**
   Farm manure.

9. **Does it matter that BOD, COD, dissolved oxygen and ammonia have not been defined previously?**
   These are defined in the tutors guide and could be given out or the students sent to look them up.

Session Plans

These are examples of schemes of work and show the flexibility of the case study.

SESSION PLAN for 2 three-hour workshops.

Objective	To think critically about the possible sources of pollution. To determine the source(s) of disperse pollution. To request analysis to identify the nature of the pollution.
Workshop 1 Part A	1. Overall aims of the case study are described. 2. Students are divided into groups. 3. The students are given the letters and from these consider whether the complaint from Arthur Pickles of Beauport Angling Association should be investigated. 4. The *'map of Midshire'* and the '*land-use along the Coley River'* are handed out.
Task 1	• The survey the land-use between Coley Bridge and Atwood is divided up between the groups. Each group is given an overhead transparency to report back with. May need to provide access to sources of information.
Part B	1. The students report back the results of their part of the land-use survey to the class. 2. The students are given the historical data from the monitoring stations.
Task 2	• Students request suitable analysis.
Part C	1. The students are given results of requested analysis.
Task 3	• Students consider what could be source of organic pollution(s).
Objective	To consider the recent data from the monitoring stations. To sample the river and request suitable analysis. To identify the nature of the pollution. To propose suitable further actions and remediation. To appreciate the importance of analytical chemistry in an environmental setting. To reflect upon their group and individual work. To understand that not all situations have neat solutions.
Workshop 2 Part A	1. The students are given the *'recent data from the monitoring stations.'* 2. The students are given *'the map between Coley Bridge and Atwood'*
Task 4	• Choose three sampling points
Part B	1. The students are given the results at the three sampling points that they have requested. 2. They consider and discuss the results obtained to decide what further sampling / analysis is required.
Task 5	• Choose three further analyses on three samples including water, fish or sediment. • Prepare a short oral presentation (optional)
Part C	1. The students are given the three sets of results requested. 2. Consider and discuss the results obtained. 3. The tutor leads the debriefing.
Task 6	• Write the group report on the findings of the investigation.

SESSION PLAN for 3 two-hour workshops.

Objective	To think critically about the possible sources of pollution. To determine the source(s) of disperse pollution. To request analysis on to identify the nature of the pollution.
Workshop 1 Part A	1. Overall aims of the case study are described. 2. Students are divided into groups. 3. The students are given the letters and from these consider whether the complaint from Arthur Pickles of Beauport Angling Association should be investigated. 4. The *'map of Midshire'* and the '*land-use along the Coley River'* are handed out. 5. The students are given the historical data from the monitoring stations.
Task 1	• (Optional) Organic analysis exercise. • Students request suitable analysis.
Part B	1. The students are given results of requested analysis.
Task 2	• The students survey the land-use between Coley Bridge and Atwood. Each group is given an overhead transparency to report back with. May need to provide access to sources of information. • Students consider what could be source of organic pollution(s).
Objective	To consider the recent data from the monitoring stations. To sample the river and request suitable analysis.
Workshop 2 Part A	1. The students report back the landuse survey. 2. The students are given in their groups the *'recent data from the monitoring stations.'* 3. The students are given *'the map between Coley Bridge and Atwood'*
Task 3	• (Optional) sampling exercise. • Choose three sampling points
Part B	1. The students are given the results at the three sampling points that they have requested. 2. They consider and discuss the results obtained to decide what further sampling / analysis is required.
Task 4	• (Optional) Inorganic analysis exercises. • Choose three further analyses on three samples including water, fish or sediment.
Objective	To consider the implications of the results. To propose suitable further actions and remediation. To appreciate the importance of analytical chemistry in an environmental setting. To reflect upon their group and individual work. To understand that not all situations have neat solutions.
Workshop 3	1. The students are given the three sets of results requested. 2. Consider and discuss the results obtained. 3. Prepare and give an oral presentation on their findings. 4. The tutor leads the debriefing.
Task 6	• Students hand in the summary of results and written report.

SESSION PLAN for 5 one-hour sessions.

Objective	To think critically about the possible sources of pollution.
Session 1 Part A	1. Overall aims of the case study are described. 2. Students are divided into groups. 3. The students are given the letters and from these consider whether the complaint from Arthur Pickles of Beauport Angling Association should be investigated. 4. The *'map of Midshire'* and the '*land-use along the Coley River'* are handed out.
Task 1	• The students survey the land-use between Coley Bridge and Atwood. Each group is given an overhead transparency to report back in the next session.
Objective	To determine the source(s) of disperse pollution. To request analysis on to identify the nature of the pollution.
Session 2 Part A	1. The students report back the results of their part of the land-use survey to the class. 2. The students are given the historical data from the monitoring stations.
Task 2	• (Optional) organic analysis exercise. • Students request suitable analysis.
Part B	1. The students are given results of requested analyses.
Task 3	• Students consider what could be source of organic pollution(s).
Objective	To consider the recent data from the monitoring stations. To sample the river and request suitable analysis.
Session 3 Part A	1. The students are given the *'recent data from the monitoring stations.'* 2. The students are given *'the map between Coley Bridge and Atwood'*
Task 3	• (Optional) Sampling exercise. • Choose three sampling points.
Part B	1. The students are given the results at the three sampling points that they have requested. 2. They consider and discuss the results obtained to decide what further sampling / analysis is required.
Task 5	• (Optional) Inorganic exercise. • Choose three further analyses on three samples including water, fish or sediment.
Objective	To consider the recent data from the monitoring stations. To sample the river and request suitable analysis. To propose suitable further actions and remediation.
Session 4	1. Consider and discuss the results obtained. 2. Start the preparation of the report and presentation.
Task 6	• Decide the source(s) of the pollution. • Consider methods of remediation. • Prepare an oral presentation, one page summary of results and written report.
Objective	To present their results. To appreciate the importance of analytical chemistry. To reflect upon their group and individual work. To understand that not all situations have neat solutions.
Session 5	1. Students hand in the summary of results and written report. 2. Oral presentation. 3. The tutor leads the debriefing.

Tales of the Riverbank Explained

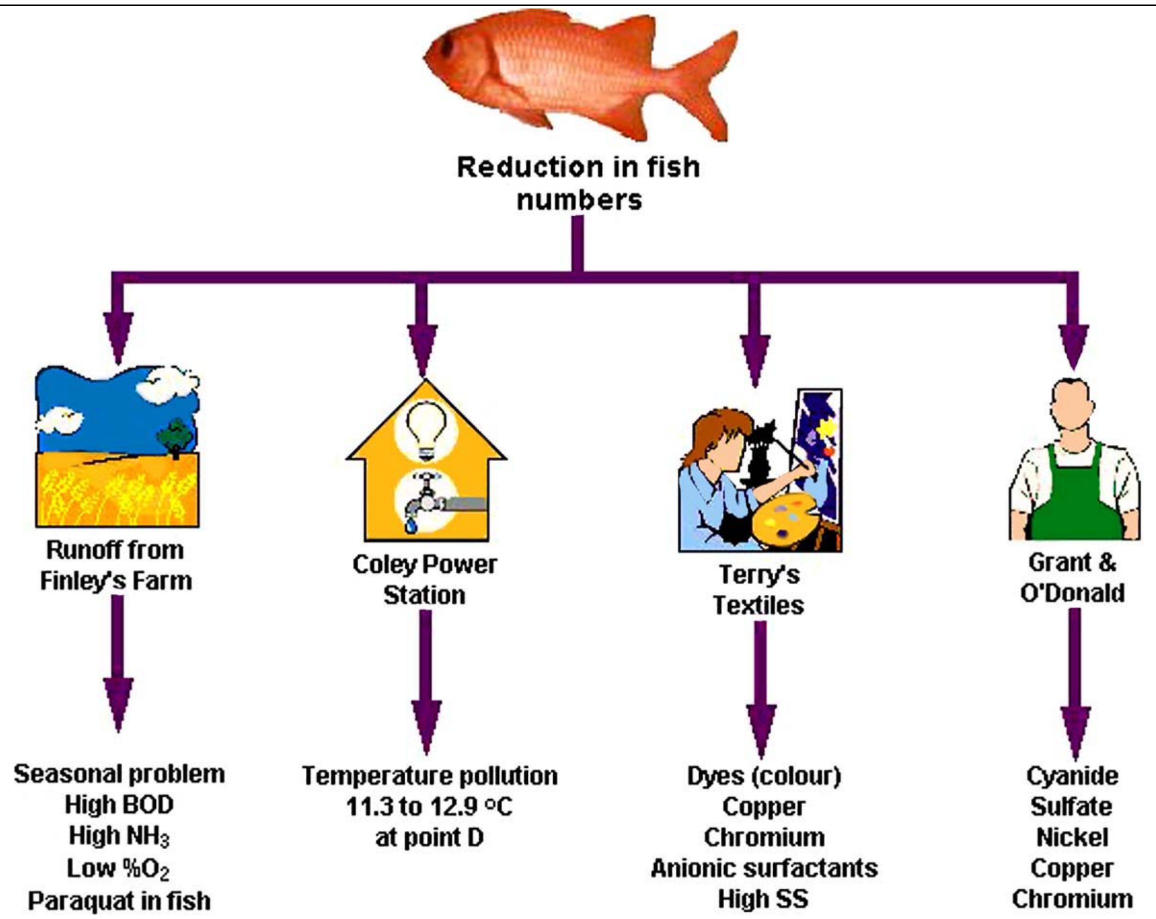


Figure 2: Tales of the riverbank explained.

The reduction in fish numbers is due to an accumulation of problems that cannot be blamed on one source.

Organic

The historical data that relates to the area between the town of Atwood (point 2) and Coley Bridge (point 3) needs investigating because of the increase in biological oxygen demand (BOD) and ammonia. Both of these are indicators of organic pollution such as runoff from agricultural land, discharge from sewers etc.

This problem with BOD, ammonia and dissolved oxygen is seasonal and occurs during the winter. This seems to suggest discharge from the land agrivated by higher precipitation and lower ground cover.

The precise source of pollution cannot be proved directly because it is the wrong time of year. Therefore, other indicators need to be tested other than water. Sediments could be tested but this is very expensive and time consuming.

Biological indicators are very sensitive to changes in their environment. Fish were caught at the Coley Bridge. The tolerance of various fish to changes in their environment is very important.

Paraquat (a herbicide) is shown as increasing in fish. This could be used as a marker to indicate that there has been an increase in runoff from the land, probably Finley's Arable Farm. This had changed to spreading manure rather than inorganic fertiliser. The discharge of grey water sewers cannot be fully discounted, as this can be a problem with the increased precipitation during the winter.

Inorganic

Recent data indicates that currently there is no problem with dissolved oxygen or nitrogen levels but there is high conductivity.

Sampling at various points between Atwood and Coley Bridge narrow down the area where the pollution could have entered the river. Students request analysis and from this are able to deduce that there has been a discharge from both or either of Grant and O'Donald Ltd. and Terry's Textiles Ltd.

pH: Any reduction in pH is buffered because it is a hard water area. Therefore any discharge of acid from the factory upstream would be masked.

Anions: The presence of cyanide at points J and L is certainly from metal plating tanks. The sulphate may have been from the plating or pickling tanks. Both probably originate from Grant and O'Donald Ltd.

The high levels of orthophosphate at points J and L are probably from Terry's Textiles from the washing of the wool.

Higher nitrate levels at points E and K are possibly due to runoff from farmland.

Anionic detergents above 500 mg/l were found at points G, J and L.

- The higher levels at Point G is probably due to discharge from the manufacture of industrial cleaning products by Harmony Cleaning Products Ltd.
- The higher levels at Points J and L are probably due to the cleaning of wool by Terry's Textiles Ltd.

Cations: There has been ten fold or more increase in the levels of nickel (1 to 76 ppb) copper (<1 to 30 ppb) and chromium (<1 to 29 ppb) at point L compared to point 2. Six-fold increases of these elements are also seen in fish.

- Chromium, copper and nickel are used in the plating industry.
- Chromium and copper salts are present in many dyes and pigments,

The increase in cadmium (118-175 ppt) and zinc (256 to 450 ppb) at point H compared to point 2 could be due to impurities from the Brass Foundry.

Physical

Temperature increase around point E is probably due to the discharge of cooling water from the Coley River coal fired power station.

High-suspended solids were found at points A-G, J and L.

- Increase of suspended solids at point L is probably due to washing of wool.

Colour: Water at point J and L was slightly greenish in colour and was slightly foamy.

- If the colour was due to dyes then this could have been from Terry's Textiles.
- The colour could have been due to transition metal salts and these could have originated from either from Grant and O'Donald metal finishing or Terry's Textiles.

Slight organic odour at D and E could have been due to runoff from the farmland and eutrophication shown by the algal growth.

Conclusion

The long-term change in the fish population is probably due to the organic runoff from the land. The main suspect is Finlay's Farm who spread manure fertiliser. A change in the procedure of application would probably solve this problem. Recommendations to the farmer should be made before autumn.

The level of paraquat is not high enough to cause harm to fish. It was a useful marker to identify the likely source of pollution.

The rise in temperature caused by the discharge of warm water from the Coley River Power Station also contributed to the eutrophication of the river. This is probably a very minor pollution factor.

The sharp reduction of fish was caused by an increase in inorganic ions. The suspects are Grant & O'Donald Ltd. and Terry's Textiles Ltd (detergents). These require careful monitoring. The levels in the fish caught gave a picture of the health of the river over time. The discharge consent of these companies needs to be reviewed and improved monitoring to make sure that this does not occur again.

Summary of Industrial Wastewater Origin, Character and Treatment

	Company Name	Industry	Potential Pollution	Environmental Effect	Major Treatment and disposal methods
a.	Atwood Incinerators Ltd.	Waste disposal by incinerator	Incineration of industrial and domestic waste causes air pollution in the form of CO, CO_2, SO_2, S_2O_3, and SO_3. About 30% by mass disposed of in landfill comprises metals (Fe, Al, Pb, Zn, Cu) and refractory residues. Dioxins also present	Toxic fumes, acid rain. Heavy metals and dioxins in land fill	Disposal of ash by landfill. Electricity produced from the incineration of domestic waste.
b.	Dexter's Dairy Farm	Farm (Dairy)	Silo (undiluted with washings) BOD 50000 mg/l, COD 12500 mg/l, SS low, pH is acid. Cattle slurry: Cattle Urine 15000 mg/l BOD Cattle Dung 13000 mg/l BOD Milk parlour washings BOD 2000 mg/l, SS 1500 mg/1, total nitrogen 4200 mg/l.	Pesticides. Eutrophication caused by high ammonia and nitrate levels.	Biodegradation and oxygenation.
c.	Brady's Brass Ltd.	Brass foundry	Cr, Cu, Hg, Pb, Zn	Poisoning of fauna by heavy metals in effluent water.	Precipitation by changing the pH, filtration and flocculation of suspended solids. .
d.	Finley's Arable Farm	Farms (Arable)	Pesticides, herbicides, fertiliser and manure from leaching pr run-off. BOD 2000 mg/l, COD 1000 mg/l, SS 3000 mg/l, pH 7.5-8.5	Herbicides kill the plant life and pesticides kill the fish directly. Eutrophication and odour. PAHs, dioxins etc. from stubble burning.	Oxygenation.
e.	Beauport Beers Ltd.	Brewery (beer & lager)	Steeping and pressing of grain, residue from distillation of alcohol, condensate from silage evaporation. Also from the filling and washing of bottles and vats. High dissolved organic solids containing nitrogen and fermented starches or their products. pH usually alkaline. 200-700 l per hl of beer (500 l average) coming chiefly from bottling and from pouring beer into casks. 400-800 g BOD_5 per hl of beer after internal recovery of yeast. Bottle washing (BOD_5 200-400 mg/l and SS 100 mg/l) Washing of fermentation vats and filters (BOD_5 1000-3000 mg/l and SS 500 mg/l) Washing of storage vats (BOD_5 5000-15000 mg/l and SS <50 mg/l)	Eutrophication from the yeast residues.	Recovery, concentration by centrifugation and evaporation, trickling filtration; use in feeds.
f.	Clover Dairy Ltd.	Dairy Products	Dilutions of whole milk, separated milk, buttermilk and whey. Wastewater: BOD 1000 mg/l, COD 250 mg/l, SS 400 mg/l, and acid pH	High in dissolved organic matter, mainly protein, fat and lactose.	Biological treatment, aeration, trickling filtration , activated sludge.
g.	McNulties Crisps PLC	Food Processing (crisps)	Potato processing: BOD 2000 mg/l, COD 3500 mg/l, SS 2500 mg/l, and pH 7-8. Grease, fat and sprouting suppressant chemicals.	Eutrophication	

	Company Name	Industry	Potential Pollution	Environmental Effect	Major Treatment and disposal methods
h.	Beauville Cottage Hospital	Hospital Incinerator	Runoff or leaching from the ash from the incinerator. As Atwood Incinerator. Dioxins found in ash.	Dioxins, heavy metals in ash. Air pollution.	Disposal of ash by landfill.
i.	Harmony Cleaning Products Ltd.	Detergents	Washing and purifying soaps and detergents High in BOD and saponified soaps. Mainly washing products (sodium carbonate, tri-polyphosphates, various soaps, biodegradable detergents, bleaches, chlorine derivatives) Dissolved grease that is readily biodegradable COD High levels of grease, anionic and non-anionic detergents.	Foaming or production of scum. Solubilising of metals and organics.	Flotation and skimming, precipitation with $CaCl_2$
j.	Clay Products Ltd.	Ceramics / Brick Works	High suspended solids, possibly crystallisation reactions and chromium compounds from the drying of ware and floor washings.	Coloration of the water caused by chromium salts.	Chromium could be removed by precipitation by changing the pH and/or reduction of Cr(IV). Suspended solids separated with or without flocculation.
k.	Paperpak Ltd.	Paper and pulp	Cooking, refining, washing of fibres, screening of paper pulp. High or low pH; coloured; high suspended, colloidal and dissolved solids; inorganic fillers	High or low pH, coloration of water. High-suspended solids reduce oxygen levels.	Settling, lagoons, biological treatment, aeration, recovery of by-products.
l.	Grant & O'Donald Ltd.	Metal plating products	Stripping of oxides, cleaning and plating of metals. Acids (sulphuric and hydrochloric acids), metals (Cr, Ni, Cu, Zn), toxic (sulphates, cyanide), low volume mainly mineral matter.	Acids, metals and toxic anions.	Alkaline chlorination of cyanide; reduction and precipitation of chromium, and lime precipitation of other metals.
m.	Marples Sheep Farm	Farms (Sheep)	BOD 2000 mg/l, COD 1000 mg/l, SS 3000 mg/l, pH 7.5-8.5 Sheep dip	Sheep dip and eutrophication.	Biodegradation and oxygenation.
n.	Cole Water Authority (Gottland Water)	Drinking water treatment plant	Aluminium sulphate from the precipitation step and eutrophication from Raw Sewage	Eutrophication from raw sewage. aluminium sulphate.	Biodegradation and oxygenation.
o.	Cole River Power Station	Coal Powered Station (Coal)	Cooling waters, boiler blowdown and coal drainage. Hot, high volume, high inorganics and dissolved solids. Air pollution in the form of CO, CO_2, SO_2, S_2O_3, and SO_3. About 30% by mass disposed of in landfill comprises metals (Fe, Al, Pb, Zn, Cu) and refractory residues. Dioxins	Temperature, ashes containing dioxins and heavy metals and acidic waste.	Cooling of the water by aeration, storage of ashes, neutralisation of excess acid wastes.
p.	Terry's Textiles Ltd.	Textiles	Cooking of fibres and de-sizing of fabric. Highly alkaline, coloured, high BOD and temperature, high suspended solids.	Colour, eutrophication from high BOD.	Neutralisation, chemical precipitation, biological treatment, aeration and / or trickling filtration.

Answers to Exercises

Organic Analysis

Analyte	Colori-metric	GLC	GC-MS	HPLC	HPLC-MS	IC
2,4,6-tri-chlorophenol		GLC-FID or GLC-ECD	Yes	electrochemical detector	Yes	anionic
Acetic Acid	Yes					anionic
Anthracene		Yes	Yes	fluorescence detector	Yes	
Chloroform	Yes	GLC-FID or GLC-ECD	Yes			
Detergents	Yes					anionic & cationic
Hexachloro-benzene		GLC-FID or GLC-ECD	Yes			
Naphthalene		GLC-FID	Yes	fluorescence detector	Yes	
PAHs		GLC-FID	Yes	fluorescence detector	Yes	
Parathion herbicide		GLC-NPD GLC-FPD	Yes			
Phenol	Yes	GLC-FID	Yes	electrochemical or fluorescence detector	Yes	UV detector
Toluene		Headspace or purge trap with FID	Yes			

FID = Flame ionising detector (general purpose)
ECD = Electron capture detector (halogens, organometallics, S, P & aromatics)
NPD = Nitrogen phosphorus detector (specific for N & P)
FPD = Flame photometric detector (specific for P & S)
UV = Ultraviolet

Sampling an effluent from a Factory

1. For example discharges from sewage works, industrial discharges and illegal dumping of chemicals etc..

2. Run-off of nitrate salts into watercourses after fertiliser application.
   The emission of methane from landfill sites into the atmosphere.
   Discharge from a landfill site into the groundwater.

3. It would be an emulsion due to high organic content with high content of suspended solids. Also there would be potential foaming from discharge of surfactants. It could smell and look rather horrible from the fats and oils used in the production of the creams. It may also be coloured depending upon the dyes used.

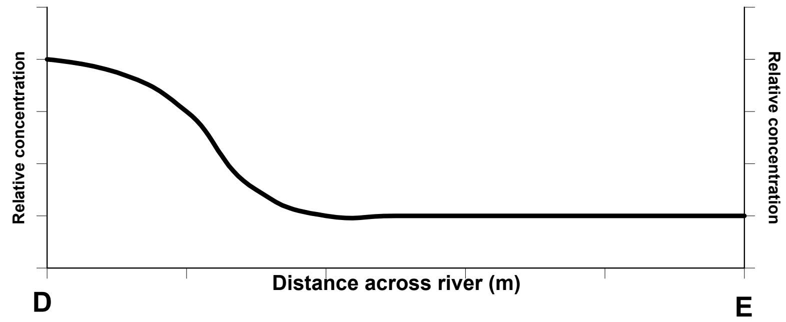
4. (a) Up-stream so the samples are not contaminated by the outflow. (A-B)

5. (b) The sample should be taken at the outflow pipe or other suitable place before the liquid discharge flows into the river.

6. Yes, the river flow data.

7. (d) The sample would be taken sufficiently far downstream from the discharge upon point to allow for dispersal. This would be up to 1km depending upon the flow characteristics of the river.

8.



9. No

Inorganic Analysis (cations)

	Titration	Colorimetry	Anodic stripping voltametry	Flame Photometer	AAS	ICP	IC cation
Al^{3+}	Yes	Yes			Yes	Yes	
Ca^{2+}	Yes EDTA	Yes		Yes	Yes	Yes	Yes
Cd^{2+}	Yes	Yes	Yes		Yes	Yes	
Cu^{2+}	Yes	Yes	Yes		Yes	Yes	
Fe^{3+}	Yes	Yes			Yes	Yes	
Hg^{2+}	Yes				hydride generation	Yes	
K^{+}				Yes	Yes	Yes	Yes
Mg^{2+}	Yes EDTA	Yes	Yes		Yes	Yes	Yes
Na^{+}				Yes	Yes	Yes	Yes
Pb^{2+}	Yes		Yes		Yes	Yes	
Zn^{2+}	Yes	Yes	Yes		Yes	Yes	
NH_4^{+}	distillation	Yes					Yes

Inorganic Analysis (anions)

	Titration	Colorimetric	Ion selective electrode	IC (anion)	Gravimetric
Chloride	By Volhards method	By mercury(II) chloranilate		Yes	As silver chloride
Cyanide	Yes	Yes		Yes	
Fluoride	By Volhards method	With thorium chloranilate	Yes	Yes	As lead chlorofluoride
Nitrate	Reduction to ammonia then distil and titrate	Yes	Yes	Yes	
Nitrite	Reduction to ammonia then distil and titrate	Diazo method	Yes	Yes	
Phosphate	Yes	Molydenum Blue or phosphovanado molybdate methods		Yes	
Sulphate	Titration of $BaSO_4$ with EDTA	Indirect (chloroanilate)		Yes	Yes with Ba^{2+}
Sulphite	Titration with iodine	Indirect		Yes	Yes with Ba^{2+} as $BaSO_4$

Useful background information

Definitions: Water Goodness Class

The quality of water depends on many parameters. It is usual to judge water quality based on its least favourable parameter.

Class IA	Water for public supply that meets the most exacting requirements and is free from pollution. Permitted use in the food industry, trout and salmon fisheries and bathing.
Class IB	Water for public supply but of somewhat lower quality. Water for fisheries other than trout and salmon, sport and amenities and livestock.
Class II	"Acceptable" quality: Suitable for irrigation and industry. It may be used for drinking after extensive treatment. Tolerable for watering of livestock. Fish may live in it with no ill effects but their reproduction may be impaired. It may be used for water sports as long as there is not excessive contact with the water,
Class III	"Mediocre" quality: Barely suitable for irrigation, cooling and leisure boating use. The water may support fish but is probably hazardous in periods of low flow and high temperatures.
Class IV	Polluted water that exceeds in any of the classes. Grossly polluted and may constitute a hazard to health and the environment.

Chemical Grading

Ammonia

Produced by the decomposition of organic material so along with BOD and dissolved oxygen are the important parameters for biological (organic) pollution (e.g. sewage, rotting vegetation).

Biological Oxygen Demand (BOD)

The five-day BOD test (BOD_5) measures the amount of organic material of biological origin that can be readily broken down by micro organisms.

Chemical Oxygen Demand (COD)

COD includes substances that both chemically and biologically oxidised so is always higher than BOD. The COD: BOD ratio varies from 1.25 to 2.50 depending upon the readily oxidiseable organic content.

Conductivity

The nature of the water depends mainly upon the geology. However, atmospheric deposition and human activity contribute.

Dissolved Oxygen (DO)

As temperature increases the saturation concentration decreases. Also, an increase in the concentration of dissolved salts lowers saturation levels in fresh water.

$$\% \, O_2 \text{ saturation} = \frac{[O_2] \text{ in water at temperature A}}{[O_2 \text{ at saturation}] \text{ at temperature A}} \times 100\%$$

Table 4: Chemical grading of rivers.

Criteria	Class IA	Class IB	Class II	Class III	Class IV
NH_3	0.4 mg/l	0.9 mg/l	2.0 mg/l	10.0 mg/l	>10.0 mg/l
BOD_5	3.0 mg/l	5.0 mg/l	10 mg/l	17 mg/l	>17 mg/l
COD	5.0 mg/l	10 mg/l	20 mg/l	30 mg/l	>30 mg/l
Conductivity	450 µS/cm	750 µS/cm	1500 µS/cm	3000 µS/cm	>3000 µS/cm
DO	>90%	70-90%	50-70%	30-50%	<30%

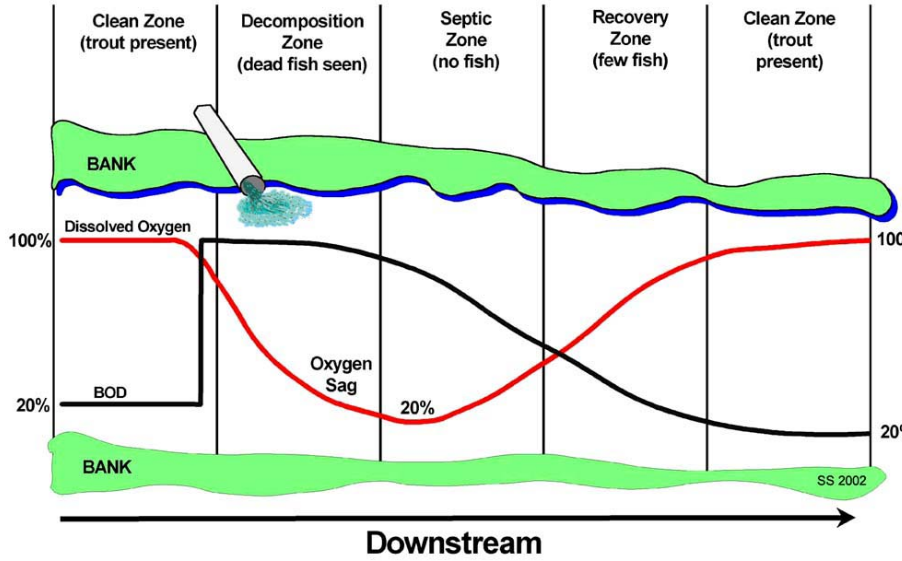


Figure 3: The ecological impact of oxygen depletion in a river.

Bio-Concentration

Some pollutants concentrate at a particular location or within organisms away from the initial source. Un-dissolved organic material precipitates onto any available solid. Hence, bioaccumulation occurs in sediment filtration organisms (muscles, scallops) or bottom dwelling fish. Toxins increase in concentration as we proceed up the food chain. Chlorinated compounds (e.g. DDT, dieldrin, PCBs etc.) are slow to metabolise and so are of great environmental concern.

Biological Grading

Some animals and plants are more sensitive to pollution than others, so the variety and number of animal and plant life is measured.

Table 5: Biological grading

	Class IA	Class IB	Class II	Class III	Class IV
Pollution Status	Unpolluted	Unpolluted	Slight Pollution	Moderate Pollution	Heavy Pollution
Biodegradable organic wastes	Absent	Absent	Absent	Advance stage of mineralisation	Heavy load
Silting of the bottom	None	None	May be light	May be considerable	Heavy & commonly anaerobic
Algae	Diverse communities not excessive in abundance	Moderate to abundant development s	Abundant	Abundant. May completely blanket riverbed	Ranges from abundant to none
Fish	Spawning ground for Salmon	Numerous types of fish	Numerous types of fish	Coarse fisheries. Unlikely to support game fishing.	Fish absent or only sporadically present.

Fish Zones

All aquatic organisms require oxygen. Specific species of fish are good indicators of water quality. The species found depends upon suitable breeding sites (e.g. gravel substrate, dense macrophyte growth, rapid flow), oxygen concentration and appropriate food supply. Rivers can be classified by zones that may or may not be repeated throughout its length.

Table 6: Fish Zones

	Trout zone	Minnow zone	Chub zone	Bream zone
Characteristic species	Trout, Bullhead	Perch, Minnow	Roach, Pike, Chub	Carp, Tench, Bream
Influence of % O_2 saturation	Likely to be excluded if less than 100% saturation	Do not require 100% saturation.	Require only 60-80% saturation.	Fish survive 30-40% saturation for long periods.
Dissolved O_2	Minimum of 7-8 mg/l	Can live for periods of weeks at 6-7 mg/l but need more O_2 to breed.	Can tolerate very low dissolved O_2 and live at 3 mg/l for long periods.	Can live for short periods down to 1mg/l
Position	Headwaters			Lowland end

References

Analytical Chemistry

Dean J.R. (1997), *Atomic absorption and plasma spectroscopy*, ACOL, J. Wiley & Sons Ltd.

Fowlis I.A. (1995), *Gas Chromatography*, ACOL, John Wiley and Sons Ltd.

Harris D.C. (1999), *Quantitative Chemical Analysis,* 5th Edition, W.H. Freeman and Company, New York

Helrich K. (1990), *Official Methods of Analysis of the Association of Official Analytical Chemists*, 15th Edition*,* Volume 1 and 2, Association of Official Analytical Chemists, Arlington, Virginia.

Howard A.G. and Statham P.J. (1993), *Inorganic Trace Analysis: Philosophy and Practice,* John Wiley & Sons Ltd.

Jeffery G.H., Bassett J., Mendham J. and Denney R.C. (1989), *Vogel's Textbook of Quantitative Chemical analysis*, Longman Scientific and Technical, Harlow

Lindsay S. (1992), *High Pressure Liquid Chromatography,* 2nd edition, ACOL, John Wiley and Son Ltd.

Lough W.J. and Wainer I.W. (1996), *High Performance Liquid Chromatography: Fundamental Principles and Practices,* Blackie Academic, London

Meyers, R.A. (Ed.), (2000), *Encyclopaedia of Analytical Chemistry: Theory and Instrumentation,* Volumes 1-15, J. Wiley and Sons Ltd., Chichester, London.

Townshend A. (1995) *Encyclopaedia of Analytical Science*, Volumes 1-10, Academic Press, London

Willard H.H., Merritt L.L., Dean J.A. and Settle F.A. (1988), *Instrumental Methods of Analysis,* 7th edition, Wadsworth Publishing Company, California.

Water Analysis and Treatment

Binnie C., Kimber M. and Smethurst G. (2002), *Basic Water Treatment,* RSC, Cambridge.

Clesceri L.S., Greenberg A.E. and Eaton A.D. (1998), *Standard methods for the examination of water and wastewater*, 20th Edition, American Public Health Association.

Hunt, D.T.E. and Wilson A.L. (1996), *The Chemical Analysis of Water,* RSC, Cambridge.

Rodier J. (1975), *Analysis of Water,* John Wiley & Sons Ltd., London

Shpiguin O.A. and Zolotov Y.A. (1988), *Ion Chromatogrphy in Water Analysis,* Ellis Horwood Ltd.

Environmental Science

Fellenberg G. (2000), *The Chemistry of Pollution,* John Wiley and Sons Ltd.

Harrison (1996), *Understanding our Environment : an Introduction to Environmental Chemistry and Pollution*, 3rd Edition, RSC, Cambridge.

Harrison R.M. (2001), *Pollution: Causes Effects and Controls,* 4th edition, RSC.

Meyers, R.A. (Ed.), (1998), *Encyclopaedia of Environmental Analysis and Remediation,* Volumes 1-8, J. Wiley & sons.

Reeve R.N. (1994), *Environmental analysis***,** ACOL, John Wiley & Sons

Russel CA (2000), *Chemistry, Society and Environment: A New History of the British Chemical Industry,* RSC.

Watts S. and Halliwell L. (1996), *Essential Environmental Science: Methods and Techniques,* Routledge

White I.D., Mottershead D.N. and Harrison S.J. (1992), *Environmental Systems: An Introductory Text*, Stanley Thornes Ltd.`

Department of Environment, Food and Rural Affairs: http://www.defra.gov.uk/

Environmental Agency http://www.environment-agency.gov.uk/

US Environmental Protection Agency http://www.epa.gov/

Yorkshire Water Authority http://www.yorkshirewater.com

Toxicology

Budadavari S. (1996), *The Merck Index: an Encyclopaedia of Chemicals, Drugs and Biologicals*, 12th edition, Merck and Co. Inc., New Jersey.

Duffus J.H. and Worth H.G.J. (1996), *Fundamental Toxicology for Chemists,* RSC, Cambridge.

Luxon S.G. (1992*), Hazards in the Chemical Laboratory*, 5th Edition, RSC, Cambridge

Ostrander G.K., ed. (1996), *Techniques in Aquatic Toxicology,* CRC Press, New York

Richardson M.L. and Gangolli S. (1992-1994), *The Dictionary of Substances and their Effects*, Volumes 1-7, RSC, Cambridge.

Walker C.H., Hopkin S.P., Sibly R.M. and Peakall D.B. (1996), *Principles of Ecotoxicology*, Taylor and Francis Ltd.