ATLANTIC SALMON TRUST

WATER QUALITY
FOR SALMON AND TROUT

JOHN SOLBÉ

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ZONATION OF FISH IN W. EUROPE

Slope (‰) of a typical 3-m wide stream

Slope (‰)	Name of zone	Substrate	Temperature	Diss. O_2	NOTES
25	TROUT	Large stones / gravel			Plants: algae on rocks, mosses in splash zone. Transporting zone
7.5	GRAYLING	Gravel / sand			Plants: as above plus species with finely divided leaves
3	BARBEL	Sand / silt			Plants: broad-leaved species can survive. Deposition zone
1	BREAM	Silt / mud			Plants: even water lilies can colonise

FOREWORD

Pollution of some of our rivers by factory wastes and untreated sewage was a sad legacy of the industrial revolution. Notable improvements have been achieved since the war, as exemplified by the River Thames, whose stench offended my nostrils in the thirties. These improvements have been offset in recent years by a more widely spread, and oftimes insidious, deterioration due to the disappearance of much of our wetlands and to changes in farming. Bigger herds of intensively reared cattle have increased the dangers to rivers from the storage and disposal of dung. The swing from hay to silage has created a new hazard - highly polluting silage liquor. Increased use of fertilizers has resulted in more being leached into rivers. Ever more abstraction from rivers has made matters worse by raising the concentration of pollutants.

Society is becoming conscious of the need for action and of its obligation to safeguard the cleanliness of rivers, rivers in whose waters plants and animals should be able to thrive. Salmon and trout, rather like the miner's canary, are sensitive indicators of pollution. Where they abound, water quality is good. Where populations have declined, or disappeared, all too often, the cause is pollution.

The intricacies of water quality are not well understood by the public, nor even by the angler and his like, who have suffered as a result of the ravages of pollution. We in the Atlantic Salmon Trust felt that we would be satisfying a need by getting an expert to write about water quality, pollution and how these affect salmon and trout throughout their fresh water life-cycle. The expert competent in both water quality and fisheries sciences is a rare breed. We count ourselves indeed fortunate in having persuaded John Solbé to write this excellent booklet. I commend it to you.

Ernest Woodroofe
Chairman, Honorary Scientific Panel

FOREWORD TO SECOND EDITION

Water Quality for Salmon and Trout was first published in 1988 and was an immediate "best-seller". This was because John Solbé has the ability to tell the layman in simple terms of the water quality requirements of salmonid fish and how these are affected by various types of pollution. This has been done in the framework of the ecology of freshwaters which thus leads to a better understanding of how pollutants disrupt the natural processes.

In this Second Edition, produced due to public demand, John has updated certain sections and included details of a group of relatively new pollutants which are likely to cause some concern. These are xenobiotic oestrogens (xenobiotic means foreign to or new to nature). There was concern that something contained in domestic sewage effluents might be having an effect on reproduction in fish. Two likely substances which could be responsible are alkyl phenols and human oestrogens. However, as John says, the effects these may have on the long-term success of a fish population is purely speculative.

Our attention is drawn to the most important factor controlling the effects of pollution discharges on fish, namely water quantity which influences dilution rates. Polluters have to meet certain standards for discharge of their wastes and these are based on the level of dilution that can be expected when released to the river. The apparent change in rainfall pattern, with drier summers and water shortages now being the norm, is going to have a profound effect on dilution of pollutants at a critical time of the year when water temperatures are high and levels of dissolved oxygen are low. This is a problem which may be difficult to address. It is up to all of us to act as watchdogs and ensure that the Agencies given the responsibility to maintain water quality are kept up to the mark.

Derek Mills
Chairman, Honorary Scientific Advisory Panel

WATER QUALITY FOR SALMON AND TROUT

JOHN SOLBÉ

The significance of water quality for the conservation of salmon and trout

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1. INTRODUCTION

What do we mean by the term *water quality*? Which aspects of water quality are important to salmonid fish? How do these factors operate through the life-cycle of salmon or trout?

This booklet attempts to explain the answers to these questions in terms that are satisfactory to both the layman and the non-specialist scientist. The first step is to give a brief description of certain physical and chemical attributes of clean water. This description may be found in Section 2 and is mostly concerned with fresh water but concludes with a note on estuarine waters. Where it is felt that a more detailed account of some feature may interest readers, this detail is given as a footnote; this technique is employed in later Sections too. Section 3 then considers the water-quality requirements of salmonids in general and at specific points in their life-cycle. With this introduction to the characteristics of clean water and the needs of fish, the reader can proceed to Sections 4 and 5, which essentially describe how things go wrong. (Section 4 is "Causes of deterioration in water quality" and Section 5 is "The effects of pollutants on fish".) At worst these *effects* are a "fish kill" but there are many other more subtle biological signals that all is not well in a body of water, and Section 6 describes some of these "biotic indices". Finally, we should not leave the subject of water quality without giving an account of the administrative provisions in force nationally and throughout the European Union, and the various useful guidelines, not part of legislation, that have been prepared to assist in defining standards to safeguard fresh water life.

2. WATER "CHEMISTRY"

2.1 Fresh Waters

This section is going to deal with some of the fundamental properties of fresh waters. It will not dwell on such physical characteristics as the density or specific heat of water[(Note 1)], although such matters are important to the well-being of fish. Nor will it describe polluted water, for which see Sections 4 and 5. However, it would be wrong to think that the best

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[(Note 1)] It is of the greatest importance to aquatic life that water is less dense at its freezing point than at higher temperatures. Thus ice floats, covering lakes with an insulating layer and reducing further heat losses to the atmosphere, which might otherwise result in a lake freezing solid. Moreover, the density of water is high enough for it to be an excellent supporting medium, while it does not create much friction to swimming animals. Its specific heat (the amount of energy required to heat a given volume) is such that it acts as a good heat-storage system. Lastly, for our purposes here, water is a first-rate solvent, able to carry a wide variety of solid or gaseous substances in solution.

water is *pure* water: distilled water is not a recommended medium! Even *clean* water is a mixture of solutions of various naturally occurring salts, the exact composition depending on the type of rock and soil over which the river is flowing and the distance travelled over those soils.

Many of the physical and chemical characteristics of water are interrelated. To set the scene for the rest of Section, these relationships will be briefly described. Figure 1 represents them.

In a "classical" or "text-book" river we expect to see the steepest gradients at the greatest altitude, the river flattening out as it approaches the sea. Of course many rivers behave in an entirely different fashion, running for much of their course over flat land until they fall abruptly into the sea, but for the purpose of illustration we can consider what happens in a text-book example. The gradient of the stream bed dictates the velocity of the water[Note 2], and the velocity, with the shape of the river bed, largely controls the turbulence of the water, and thus the composition of the stream bed (its *substrate*). In fast-moving, turbulent water, as at high altitude, only boulders can resist the force of the water. As the water moves down the slope, and the gradient lessens, so do the velocity and turbulence, so that the substrate becomes progressively one of smaller stones, gravel, sand, silt, and mud. Since conditions are never uniform we can expect to see patches of gravel or small stones, suitable for salmonid redds, at various points down a river system and not just confined to a small stretch near the torrential headwaters. Turbulence plays another important role: it has a major effect on the speed at which the water can exchange gases with the atmosphere at the water surface. The "reaeration coefficient", a factor which sums up the effect of turbulence on this exchange, is discussed further in Section 2.1.1.

Naturally, water a high altitude is cooler than water in the lowlands. Temperature (see Section 2.1) controls the amount of oxygen which a body of water can hold. Obviously too the distance that water has travelled from its source is also related to altitude. As the water travels towards the sea it dissolves elements from the soil and bedrock, depending on

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[Note 2] Velocity and flow are not the same thing. Velocity is speed, described as metres per second (m/s) while flow is volume carried past a point in unit time. Flow is therefore given as cubic metres of water per second, or "cumecs" (m^3/s). Some conversions may be useful:

$$1 \text{ m/s} = 2\frac{1}{4} \text{ mph}$$
$$1 \text{ m}^3/\text{s} = 19 \text{ million gallons per day (mgd)}$$
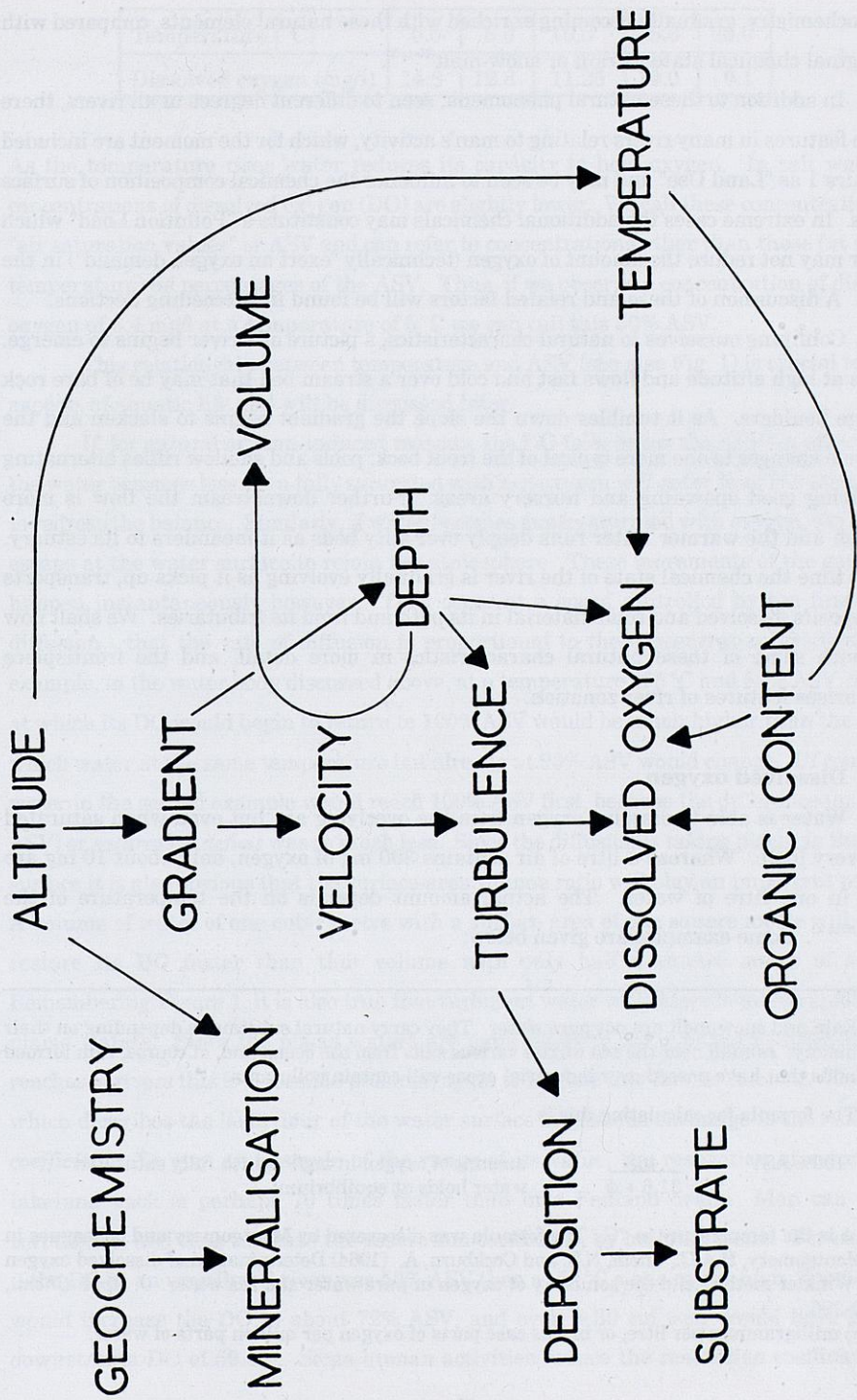
Figure 1 Diagram of some of the interrelated physico-chemical features of rivers and streams

ALTITUDE

GRADIENT

VELOCITY

TURBULENCE

DISSOLVED OXYGEN

ORGANIC CONTENT

TEMPERATURE

VOLUME

DEPTH

GEOCHEMISTRY

MINERALISATION

DEPOSITION

SUBSTRATE

the geochemistry, gradually becoming enriched with these natural elements, compared with its original chemical state as rain or snow-melt[Note 3].

In addition to these natural phenomena, seen to different degrees in all rivers, there will be features in many rivers relating to man's activity, which for the moment are included in Figure 1 as "Land Use" and may be seen to influence the chemical composition of surface waters. In extreme cases the additional chemicals may constitute a "Pollution Load" which may or may not reduce the amount of oxygen (technically "exert an oxygen demand") in the water. A discussion of these and related factors will be found in succeeding Sections.

Confining ourselves to natural characteristics, a picture of a river begins to emerge. It rises at high altitude and flows fast and cold over a stream bed that may be of bare rock or large boulders. As it tumbles down the slope the gradient begins to slacken and the substrate changes to one more typical of the trout beck: pools and shallow riffles alternating and giving good spawning and nursery areas. Further downstream the flow is more sluggish and the warmer water runs deeply over silty beds as it meanders to its estuary. All the time the chemical state of the river is gradually evolving as it picks up, transports and deposits dissolved and solid material in its path and from its tributaries. We shall now deal with some of these natural characteristics in more detail, and the frontispiece summarises features of river zonation.

2.1.1 Dissolved oxygen

Water is able to dissolve oxygen from the overlying air, but even when saturated holds very little. Whereas a litre of air contains 300 mg of oxygen, only about 10 mg are found in one litre of water. The actual amount depends on the temperature of the water[Note 4]. Some examples are given below:

[Note 3] Rain and snow-melt are not pure water. They carry natural substances depending on their recent history: rainfall near the sea carries various salts from the ocean and, of course, rain formed from clouds that have passed over industrial areas will contain pollutants.

[Note 4] The formula for calculating this is

$$100\% \text{ ASV} = \frac{468}{31.6 + \phi} = \quad \text{amount of oxygen in mg/l* which fully saturated water holds at equilibrium;}$$

where ϕ is the temperature in °C. The formula was discovered by Montgomery and colleagues in 1964. Montgomery, H.A.C., Thom, N.S. and Cockburn, A. (1964) Determination of dissolved oxygen by the Winkler method and the solubility of oxygen in pure water and sea water. *J. Appl. Chem.*, 14, 280-296.

* mg/l = milligrammes per litre, or in this case parts of oxygen per million parts of water.

Temperature (°C)	0.0	5.0	10.0	15.0	20.0
Dissolved oxygen (mg/l)	14.8	12.8	11.25	10.0	9.1

As the temperature rises water reduces its capacity to hold oxygen. In salt water the concentrations of dissolved oxygen (DO) are slightly lower. We call these concentrations the "air saturation values" or ASV and can refer to concentrations other than these (at a given temperature) as percentages of the ASV. Thus, if we observe a concentration of dissolved oxygen of 6.4 mg/l at a temperature of 5°C we can call this 50% ASV.

This relationship between temperature and ASV (see also Fig. 1) is crucial to many aspects of aquatic life and will be discussed later.

If, for natural or man-induced reasons, the DO fails below the ASV (in other words the water becomes less than fully saturated with air) oxygen will enter from the atmosphere to redress the balance. Similarly, if water becomes supersaturated with oxygen, oxygen will escape at the water surface to rejoin the atmosphere. These movements of the gas do not happen instantaneously however. They occur at a speed controlled by the first law of diffusion - that the rate of diffusion is proportional to the concentration gradient. For example, in the water body discussed above, at a temperature of 5°C and 50% ASV, the *rate* at which its DO would begin to return to 100% ASV would be much higher than the *rate* at which water at the same temperature but already at 90% ASV would change. Of course the water in the second example would reach 100% ASV first, because the difference (only 10% ASV) or *saturation deficit* was so much less. Since the diffusion is taking place *via* the water surface it is also obvious that the surface-area:volume ratio will play an important part too. A volume of water of one cubic metre with a surface area of one square metre will clearly restore its DO faster than that volume with only half a square metre of surface. Remembering Figure 1, it is also true that turbulent water will reaerate more rapidly than placid waters. Since the placid waters are more likely to occur in the polluted lowland reaches of rivers this is a possible problem, again to be gone into further later on. The factor which describes the behaviour of the water surface in gaseous exchange is the *reaeration coefficient*. To give an example of the range of its value, the reaeration of a turbulent lakeland beck is perhaps 70 times faster than in a Fenland drain. Man can induce turbulence, and thus increase the reaeration coefficient, by building weirs. For example, if the DO in an unpolluted river was 50% ASV then at 15°C a one-metre high, free-fall weir would increase the DO to about 72% ASV, and even a 30 cm weir would have given a downstream DO of 59.4%. Some human activities reduce the reaeration coefficient (see

Section 5.2), thus reducing the ability of an organically polluted river to obtain the oxygen needed to break down the polluting matter. The two weirs mentioned above would have been slightly less efficient in reaerating a polluted water: the one-metre weir would have given a final DO of 69% and the smaller weir 57.8%.

Rivers have another source of supply of oxygen in addition to the atmosphere: aquatic plants. Plants use solar energy to convert carbon dioxide and water to sugar in the process known as *photosynthesis* during which oxygen is given off from the plants as a waste product. Plants are not efficient at fixing solar energy: it is unusual to see aquatic plants better than 1% efficient in this respect, but their oxygen production can be very useful. For example plants in a stream with good growth supplied 8.3 grams of oxygen per square metre of water surface per day (g O_2/m^2 d) which was more than 95% of the stream's requirements (see later in this Section). The actual amount of oxygen evolved depends on a number of things, but principally the light intensity; photosynthesis ceases at night. If we observe the DO in a weedy stream during a 24-hour period, if the stream is rather placid (as it would be, or rooted plants would have been washed out) the DO is at its lowest at around dawn but then rises as light intensity increases and temperatures rise until mid-afternoon. A long decline in DO then begins. At its peak the DO may far exceed 100% of the air saturation value (ASV) (double this value is not unknown); at night the level could plummet to such low levels that animal life was threatened. In natural streams there are not normally sufficient nutrients to promote plant growth to this extent, so abnormal magnitude in DO cycles may be an indicator of 'pollution'.

But why should the DO fall below 100%? The answer is that demand for oxygen can outstrip supply. This demand is caused by the respiration of plants, animals and micro-organisms in the stream. Respiration is the process by which aerobic[Note 5] organisms oxidise their food, in order to release from the food the energy which they require for survival of the individual and thus the species. In the daylight, during photosynthetic production of oxygen by plants this respiratory demand is not apparent, but at night, after photosynthesis has ceased, respiration causes a fall in DO. Of course if the water is turbulent the main source

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[Note 5] *Aerobic* respiration is that which takes place in the presence of free gaseous or dissolved oxygen. *Anaerobic* respiration (for example that seen in methane-producing bacteria) is the liberation of energy by the breakdown of substances not involving the consumption of oxygen.

of oxygen (and the route by which excess oxygen is lost from the system) may be the water surface , and little diel [Note 6] change will be seen.

As oxygen levels alter in the stream so do other factors (such as pH: see 2.1.3) which are also linked directly or indirectly with the process of photosynthesis.

To summarise the features of dissolved oxygen in streams, oxygen can be supplied from two sources: the water surface and aquatic plants. Oxygen is demanded as a result of the respiratory activity of aerobic organisms and the supply may or may not be sufficient to maintain a satisfactory DO. Unless a stream is quite turbulent this changing balance between supply and demand can lead to diel changes in DO that are proportional to the rates of supply and demand throughout a 24-hour cycle.

2.1.2 Temperature

It must already be clear that water temperature is a very important feature of the aquatic environment. It controls the amount of oxygen that water can contain at equilibrium with the atmosphere (2.1.1) as well as such things as density (2.1), but it is also fundamental in controlling the rate of most living processes (such as the speed of development of an egg, the metabolic rate and so on).

Spring water issues from the ground at about 11°C and, depending on air temperature, either warms up or loses heat as it moves towards the sea. Springs therefore may be warmer in winter and cooler in summer than other waters.

Species of fish vary in their preference for, and ability to tolerate, various temperature ranges. Salmonids are typical of cool water species. The relevance of temperature will become apparent at various points below, and needs no further introduction here.

2.1.3 pH

To describe the degree of acidity or alkalinity of water it is convenient to use the *pH* scale. For our present purposes it is sufficient to realise that the pH of neutral water is 7.0, that for every pH unit less than 7.0 water progressively becomes ten times more acidic and for every pH unit greater than seven it becomes ten times more alkaline. Thus pH 5 is ten times more acid than pH 6 and pH 10 is 100 times more alkaline than pH 8. As with

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[Note 6] *Diel* means 'of a 24-hour period' in contrast to *diurnal* which relates to the hours of daylight and is thus the opposite of *nocturnal*. Another word for diel is *circadian*.

temperature, fish differ in their ability to tolerate extreme of pH. For most species a range of pH 5.5 to pH 9 should not be harmful in exposure periods lasting for a life-span.

Even unpolluted waters do not all have the same pH. This is because pH depends on the chemical characteristics of the water, which in turn depend on the chemistry of the underlying soils and rocks of the catchment and on the type of vegetation encouraged by the geology and climate of the catchment area. Water flowing over silicaceous rocks such as sandstones or granite is likely to have lower pH values than are to be found in streams draining chalk or limestone. If a stream is fed by water seeping out of boggy moorland it is quite likely to have extremely low pH values at times - for perfectly natural reasons. The brown colour of such waters is due to the presence of *humic acids*, which can often reduce the pH to less than four. Of course, the polluting effects of 'acid rain' may exacerbate this phenomenon (see Section 4.2.5), but it is useful to note that unpolluted rain, fully saturated with carbon dioxide, has a pH of 5.6.

As mentioned in Section 2.1.1, photosynthetic activity by plants can affect the pH of streams. During daylight, when plants are excreting oxygen and consuming carbon dioxide, the pH of a weedy stream can climb to well over pH 9. Conversely at night the continuing, but now apparent, respiration of the plants is consuming oxygen and excreting the no-longer required carbon dioxide. The carbon dioxide reacts with the water to form carbonic acid (H_2CO_3), which, although weak, is sufficient to reduce the pH of the stream to well below pH 7.

$$H_2O + CO_2 \rightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$
$$\text{carbonic}$$
$$\text{acid}$$
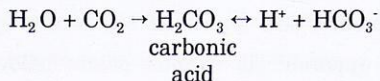
The exact extent to which these changes occur is, again, related to other chemical and physical features of the stream, such as its *buffering capacity*[Note 7] and ability to exchange gases with the atmosphere.

The way in which pH affects fish directly, or through its influence on other features of the environment, is explained in Section 5.2. For now, it is sufficient to record that pH is one of the fundamental factors operating in the chemistry of natural waters.

[Note 7] *Buffering capacity* is the ability of the stream to resist changes in pH when acids or alkalis are produced in the water. Carbonic acid has good buffering capacity.

2.1.4 Suspended solids

Within the water column of any stream or lake, particles are suspended. They may be inorganic, arising from the erosion of stream beds and banks upstream or carried into the stream from the surrounding land, or organic, owing their origin either to life processes within the stream or to processes such as leaf-fall outside the stream. Suspended solids are necessarily buoyant but may be held in suspension by the turbulent action of the water, until they reach a quieter zone where they may be temporarily or permanently deposited. Similarly, suspended material may not be made up of permanent solids: it may be degradable (broken down into simpler fragments), it may even be living (in that when we measure suspended solids we don't normally separate out living material, such as bacteria or algal cells[Note 8], from dead matter). Suspended solids are usually referred to as a concentration of dry matter filtered out from a given volume of water. Thus '25 mg/l SS' means 25 milligrammes of solid, dried at about 105°C, per litre of water.

In suspension, solids may act as sites which bacteria can colonise; they also absorb light, and if the solids are in fact algae, which need light for photosynthesis, there comes a point where they have grown so densely that they severely limit the penetration of light to their own populations and growth becomes limited as a consequence.

Once settled, the solids form a sandy, silty or muddy habitat for organisms such as worms which have evolved to take advantage of these situations. In a natural river it is expected that silt banks will form to such an extent in certain places that the channel will no longer carry the winter rains and will cover the flood-plain. One or more new channels may be cut, forming a *braided* course, or the silt banks may be swept away and the river return to its old course. Throughout Europe since the Middle Ages man has increasingly restricted rivers to single channels, which must have affected river life profoundly.

The passage of water through deposited fine solids is very much impeded. If the solids include organic material, the demand for oxygen may exceed the capacity of the interstitial water to provide oxygen at a sufficient rate. The silt may then become anaerobic (devoid of free oxygen) and a markedly different chemistry will then begin to operate (see 5).

The silt of deep waters may lie undisturbed for millenia, gradually accumulating as particles rain down from the overlying water. By carefully taking cores of these deposits one may identify the remnants of organisms that lived in or near the lake hundreds of years before. The ash from ancient major volcanic eruptions can be seen and much more recently

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[Note 8] Algae are simple plants with no roots, stems or leaves but which do contain chlorophyll. They may consist of a single microscopic cell like diatoms, or be tens of metres long, like some seaweeds.

a layer enriched in radioactive caesium may be present, resulting from the Chernobyl disaster. The layers can be dated and, for example, pollen grains or the minute silicaceous 'skeletons' of diatoms can be identified. Since the requirements or tolerances of these algae are known (by examining their living descendents) it is possible to estimate the conditions under which they lived. This 'forensic' technique has been used to follow climatic changes and the acidity or nutrient status of lakes back through time.

2.1.5 Nitrogen and phosphorus

For plants to grow in fresh waters they need a wide variety of trace elements. For example, the diatoms discussed in 2.1.4 require silicon to form the structures that support and protect their soft tissues. The two elements which are the subject of this section however are more usually termed *plant nutrients*, and the rate and mass of growth of a population of plants would be largely controlled by the concentration of one or the other (given sufficient light and no major influence of herbivorous organisms). Normally it is phosphorus which is the *limiting nutrient* for freshwater plants in the British Isles, although there will be exceptions where nitrogen, silicon, potassium or some other element plays this role.

The origins of nitrogen and phosphorus in natural waters are influenced very much by the facts that nitrogen is normally a very inert gas whereas phosphorus is a highly reactive solid[Note 9]. The combined nitrogen we see in water (nitrates, ammonium compounds etc) has largely been washed into it from the surrounding soils, and so is a mix of natural and fertilizer nitrogen, depending on the surrounding land-use. Phosphorus is so reactive that in nature it is always found combined with other elements. The mineral apatite, for

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[Note 9] Nitrogen makes up 78% of the atmospheric gases, but the majority of plants cannot utilise it in that form but take it up as nitrates or ammonium salts. The only natural deposit rich in nitrogen is the Chilean saltpetre (sodium nitrate) but soils do contain minute quantities of inorganic nitrogen in the form of ammonium sulphate and the nitrates of sodium, potassium and calcium. However, any reasonable soil contains about 7 tonnes of nitrogen per hectare - so where has it all come from? The answer, generally speaking, is that it has been *fixed* from atmospheric nitrogen by bacteria living freely in the soil or in nodules of roots of leguminous plants, like clover. It is significant for the communities of animals living in or beside rivers that the alder tree also fixes nitrogen. Alder leaves are a valuable source of food. Atmospheric nitrogen is also converted to nitrates as a result of electrical discharges such as lightning. Natural processes of decay allow the nitrogen to be recycled in the soil and an important principle of agriculture is the maintenance of soil fertility by returning the naturally fixed nitrogen to the soil as farmyard manure and until recently as human excreta (originally 'night soil', then raw sewage from sewage 'farms') and now as "sewage sludge" after treatment. Of course the needs of agriculture have outstripped the natural provision and recycling of nitrogen, and the farmer now adds ammonium sulphate or nitrate fertilizers to provide a readily-available source of nitrogen for the plant crop.

example, is calcium phosphate and this and similar compounds are found to varying degrees in rocks and soils. They dissolve slowly in water and leach into rivers. Foresters, prefer this slow release and so use *ground rock phosphate* when encouraging conifer growth (nitrogen is rarely added in forestry) but farmers need a quick-release material, *superphosphate*, and this too finds its way into streams and lakes.

Eutrophication - It is relevant to discuss eutrophication at this point, if only to emphasise that it can be a perfectly natural phenomenon, as well as being a symptom of pollution when accelerated by human activity.

All natural ecosystems[Note 10] are dynamic, changing at various rates in response to climatic or other factors. Sometimes an ecosystem reaches its "climax" state where the system stabilises. For example the climax vegetation of Southern England would generally be oak woodland on the good soils, if nature had its way. The natural end-point of a lake is to become dry land bisected by its feeder stream. It will gradually fill with eroded material from its catchment. Vegetation, building up more sediment as it grows, will encroach as the water shallows.

Pristine waters, evolving since the last Glaciation, may gradually become enriched with plant nutrients as the land surrounding them releases nitrates and phosphates. This enrichment with plant nutrients is termed *eutrophication*. The speed at which this happens depends on the natural and human utilisation of the catchment. In nature it can be very slow: the lake evolves from a state of *oligotrophy* (very little nutrient) through *mesotrophy* to the fully eutrophic condition.

The lake community reflects the trophic state of the water as the animal and plant populations express their preference for certain conditions. River communities react in the same way, but of course influenced by the fact that water may reside in a reach of river for only minutes or hours rather than its residence period of days, months or years in a lake.

The importance of nitrogen and phosphorus to salmon and trout therefore is that these two elements are principally responsible for controlling the whole basis of the ecosystem - its *primary productivity*, the trapping of solar energy by plants - and the start

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[Note 10] An *ecosystem* is made up of the non-living environment and the community which lives in it. (There is no particular size defined for any ecosystem; it could be a pond or an inland sea, a copse or an entire tropical rain-forest.)

of the chain of events which passes the energy, as food, from algae to zooplankton or benthic invertebrates[Note 11], to small fish and eventually to the top carnivores of the community.

2.1.6 Calcium, magnesium, sodium and potassium

These elements are known as the *alkali metals* (sodium, Na, and potassium, K) or the *alkaline earth metals* (magnesium, Mg, and calcium, Ca). They are so reactive that they never occur in isolation but are always combined with other elements. (Some *heavy metals* (2.1.8) such as silver or copper can be found as the free metal.)

They are all ubiquitous but will vary in concentration in water according to the geology and location. Sodium may be derived from mist and rain near the sea, as well as appearing as carbonates, nitrates and chlorides in soil. Potassium may be found as chlorides, nitrates and carbonates too. Magnesium is abundant in sea water as the chloride and, with calcium, in magnesian limestone (dolomite) and to a lesser extent in chalk. Magnesium also occurs as the sulphate (Epsom salts). Calcium sulphate is found as gypsum, and the carbonate of course is the principal component of chalk, marble and limestones.

All four metals are *essential* to living organisms. Only traces of sodium may occur in plants but it is an important part of extracellular fluid in animals, just as potassium is within cells. Potassium is needed by plants for protein synthesis, the formation of chlorophyll and the assimilation[Note 12] of carbon. Plant ash is rich in potassium carbonate. In animals potassium plays an important role in the functioning of the kidneys, among other things.

Calcium is an important constituent of plant cell walls and in animals it is vital for boney structures, the clotting of blood, the contraction of muscles and glycolysis[Note 13]. About 90% of the body ash of a vertebrate will be calcium phosphate. Magnesium is part of the chlorophyll molecule and has important roles in enzyme[Note 14] function and glycolysis.

[Note 11] *Benthic* invertebrates are those which live on, in or near the bottom of a water body. (Gr. *benthos*, depth.) *Zooplankton* are animals which float or drift in the water almost passively (Gr. *zoion*, animal; *planktos*, wandering).

[Note 12] *Assimilation* is the general term for the building up of the complex tissues of an organism from relatively simple food-stuffs or the products of digestion of food.

[Note 13] *Glycolysis*, literally 'sugar-splitting', is an initial stage of cell respiration (see 2.1.1).

[Note 14] *Enzymes* are proteins which act as biological catalysts. They speed up chemical reactions in organisms without themselves being used up, but they often require certain definite conditions if they are to perform effectively.

As well as these important functions within animals and plants, the concentrations of Na, K, Ca and Mg in the water may influence the nature and success of fish and the feeding relationships on which they depend. For example, plant growth may (but probably only rarely) be *limited* by lack of potassium. The success of molluscs and some crustaceans will clearly depend on the abundance of calcium, especially in still waters, since their shells or exoskeletons are largely formed from calcium carbonate. In polluted water the hardness, which depends to a large extent on the calcium and magnesium present, can affect the toxicity of heavy metals (see 5.2).

2.1.7 Carbonate, bicarbonate, sulphate and chloride

It will be obvious that much of what has been said above about the sources of elements in water will also apply to these *anions*[Note 15]. The underlying soils and rocks and the nearness of the sea will each influence the composition of unpolluted surface waters. The atmosphere may play an important part in these cases, supplying carbon dioxide and salts. Carbon dioxide can dissolve in water (as in rain) to form carbonic acid (2.1.3), which can itself dissolve carbonate rocks such as limestones. Chlorides from transported sea salt and sulphate from atmospheric sulphur dioxide can also, directly or indirectly, enter river systems from rainfall.

These anions provide the principal balance for the cations in fresh water, and often (chloride especially) within living tissue. They have other roles however and the provision of carbon dioxide for photosynthesis must be the most important. Most higher plants can utilise bicarbonate ions directly in photosynthesis, but mosses cannot. They have to use carbon dioxide (and find it in the splash zone of turbulent reaches without problem). Carbon dioxide can be very rare at times in hard-water streams with abundant plant growth, particularly in the daytime. The plants take up CO_2 as well as bicarbonate but without a certain amount of CO_2 bicarbonate cannot remain in solution. Instead it is converted to calcium carbonate which precipitates, sometimes to the dramatic extent seen in formations of *travertine*. The carbonate/bicarbonate balance is a far more dynamic balance than is seen in any other fresh water anions. It changes from day to day and particularly from hour to hour as the result of photosynthesis.

[Note 15] Molecules can break apart in water to form ions - anions and cations. *Anions* are negatively charged ions, so we should write carbonate as $CO_3^=$ with two negative charges and bicarbonate as HCO_3^- with one negative charge etc. *Cations* are positively charged ions.

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2.1.8 Heavy metals

No substance is entirely insoluble in water but the concentrations of many heavy metals may be minute. Once again the metals and concentrations observed will depend on the geology and weathering processes of the area and on the characteristics of the metal concerned. For example, lead is comparatively insoluble so that even in water at an alkalinity of 50 mg/l $CaCO_3$ and pH 6.5 a saturated solution would contain only <200 µg/l, that is, less than 200 parts in one thousand million.

In nature metals are associated with igneous and metamorphic rocks or in veins in a wide variety of hard rocks (as in the west of Britain - tin in Cornwall, copper on the Devon/Cornwall border, lead, gold and silver in Wales, and lead in the Lake District). The major exception is iron, which is found in the limestones of Northamptonshire, in concentrations which made it worth mining until recently.

Of course metals, like any other materials, get redistributed by erosion and transport by water, wind and ice. They may become concentrated in the process: a good example is the muds of the estuaries of the South West where, partly due to man's activities inland, considerable masses of heavy metals may now be found. Drainage from coal mines, often ferruginous, and the iron rich soils below many peaty deposits, are also evidence of concentration.

Some metals are essential to living organisms; all are toxic if concentrations are high enough.

In plants, iron, Fe, manganese, Mn, and copper, Cu, are all tied up with respiration. Iron, and possibly copper, is important in the formation of chlorophyll. Zinc, Zn, is needed by all plants. Molybdenum, Mo, is essential to nitrogen-fixing plants (see Note 9 in Section 2.1.5) and may be needed by any plant where the only source of nitrogen is nitrate. Vanadium, V, cobalt, Co, and silicon, Si, are found in all plants but generally their role has not been defined.

In animals, iron is part of the haemoglobin molecule and *cytochromes* (proteins containing a pigment and essential to various stages of respiration). Manganese and molybdenum activate enzymes. Copper is needed to catalyse the use of iron but neither metal can function without the presence of cobalt (which is found in vitamin B12). Zinc is part of the carbonic anhydrase molecule. This enzyme splits carbonic acid into water and carbon dioxide, reversing the first part of the equation shown in 2.1.3. The particular importance of this to the effect of ammonia on fish is discussed in 5.2.3. Zinc is also necessary if insulin is to function.

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Aluminium, Al, arsenic, As, nickel, Ni, and silicon seem to be present in all animals but if they have a beneficial role this has not yet been described.

Aquatic organisms will derive their metal requirements from their food and from the dissolved or finely divided metallic substances in the water. They may have the ability to store metals until they need them. This can be useful if they encounter excessive concentrations, as in a polluted environment, because it can offer some protection from toxicity. Section 5.2 discusses this further, and the metal requirements of fish are listed in Section 3.1.5.

A metal dissolved in water can take one or more of a number of forms, depending on the water chemistry. These forms are called *species*. The species which occur depend on such other characteristics of the water as pH (very important), the presence of other dissolved substances, temperature and the 'age' of the water; (in other words there is an equilibrium situation which will arise in a given mix of water and metal salts, but it takes time to develop)[Note 16].

The importance of this will be demonstrated later: the toxicity of metals to aquatic organisms is very much dependent on the species of metal present, in the same way that the toxicity of ammonia is a function of the concentration of the species NH_3, unionised ammonia, while all other species, such as the ammonium ion, NH_4^+, have negligible toxicity.

2.2   Estuarine Waters

Estuaries have a special place in any consideration of the *anadromous* salmonids or the *catadromous* eel[Note 17].

Estuarine waters may vary considerably in quality within the 12 hours and 25 minutes of a tidal cycle. The water may be almost fresh at low tide and yet have the salinity of full sea water at high tide. Turbidity and oxygen concentration may also vary with tidal state, while in a nutrient-rich estuary, regardless of tidal state, the effects of algal photosynthesis and respiratory oxygen demand may cause concentrations of dissolved oxygen to fluctuate so much that salmonids are placed at risk, especially at night when dissolved oxygen may become very scarce.

[Note 16] As an example we can consider aluminium: at a pH of 4 most dissolved aluminium in water is likely to be the species Al^{+++}. In terms of the hydroxides, as the pH rises there is a progression through $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$ and finally at pH 8 almost all the dissolved aluminium would be in the form $Al(OH)_4^-$.

[Note 17] *Anadromous* fish are those which ascend rivers to spawn. *Catadromous* species migrate to spawn in the lower reaches of rivers or the sea. (Greek *ana*, up, *dromos*, a run; *kata*, down.)

The presence of so much dissolved material when the estuarine water is saline can completely alter the chemical state of the heavy metals (for example) so that rules for the behaviour of such elements in fresh water give little guide to estuarine chemistry. One of the properties of saline water is that it tends to flocculate the finely divided solids entering the estuary from its river. The flocculated solids can then settle out: estuaries are often muddy places as a consequence.

As the previous section indicated, estuaries, like lake sediments, can act as pollutant *sinks*, accumulating materials reaching them from their rivers and the sea.

The salinity of an estuary can change rapidly from that of fresh water to sea water[Note 18]. This has profound effects on the organisms living in or passing through estuaries. The salinity of the blood of a fish, both freshwater and marine species, is roughly equal to one-third strength sea water. Natural forces would tend to equalise the strength of the salt solutions inside and outside the fishes body. This would mean that the marine fish would lose water, causing the concentrations of salts to rise in its body until they reached the same strength as sea water. Conversely the freshwater fish would gain water until the salts in its body were reduced in concentration until they reached the strength of fresh water. In both cases the body fluids would be at the wrong strength to allow metabolic functions to be performed. Protective mechanisms have therefore evolved to maintain the correct salt balances, and it is fascinating that these mechanisms not only work for the species which remain the whole of their lives in one type of water but can also cope with the needs of a migratory species as it moves from marine to fresh waters, or *vice versa*.

3.   WATER QUALITY REQUIREMENTS OF SALMONID FISH

3.1   General

One can approach the question of the water quality requirements of fish from two points of view - the positive qualities of a water which must be present for salmonids to be successful, and deleterious qualities which must be avoided.

Naturally there will be several classes of substances or condition to consider:

(i)   essential elements without which fish would die sooner or later;

[Note 18] Salinity is usually expressed as parts of sodium chloride per thousand parts of water. Full sea water has a salinity of about 35 parts per thousand (35 ppt or 35‰).

(ii) non-essential elements which in too high a concentration will become poisons (as will even essential elements of course);

(iii) elements which affect the value of the essential elements or modify the toxicity of poisons;

(iv) environmental features other than substances, which control or influence the external or the internal environment of the fish.

This section is devoted to the positive qualities of water for salmonids. As such it touches on classes (i), (iii) and (iv). The negative qualities, in effect pollution, are dealt with in Section 5.

All the substances or conditions mentioned here have already been considered in Section 2 as characteristics of surface waters. Here six essential factors are discussed from the general point of view of fish, while in 3.2 the needs of individual life cycle stages are listed.

3.1.1 **Dissolved oxygen**

Fish need oxygen at every stage in the life history in order to respire. Respiration was briefly explained in Section 2.1.1. The amount of oxygen required by a fish is not constant however. It changes as the fish grows: one kilogram of resting fish (in other words fish demonstrating *basal metabolism* or 'tick-over') at 10°C may require just under 300 mg oxygen per hour *if the kilogram consists of 100 small fish*. Fish ten times larger only use 200 mg oxygen per kilogram hour. If the kilogram consists of just one fish the consumption is only about 160 mg O_2/hr. The same phenomenon is seen in warm-blooded animals and the explanation here is readily understood - a small animal has a larger surface area:volume ratio than a large animal. It thus loses heat more rapidly and this increases its need to "burn" food to maintain its body temperature at the level essential for its various physiological systems to operate. But a fish is 'cold-blooded'. Its temperature is 'the same as' its external environment - the water, ... isn't it? In fact the fish *is* producing heat as it breaks down its food but the water, being such a good conductor, and the fish having so little insulation, result in the excess heat being removed almost as rapidly as it is generated. So the deep body temperature of a fish is almost that of the surrounding water. There are

exceptions: the tunny, when swimming fast, may have an internal temperature that is 12 degrees C[Note 19] higher than the temperature of the sea.

So, as a fish increases its activity it requires more energy and its metabolic rate increases, as does its oxygen consumption. The same thing happens if the cause of the increase in metabolic rate is not activity but a rise in temperature. The 100-gram fish whose oxygen consumption was 200 mg/kg hr in the example above (at 10°C) would need twice the oxygen at 20°C and half the oxygen at 5°C[Note 20].

Different species of fish need different concentrations of oxygen and their blood chemistry has evolved to enable them to live successfully, for example, only in well-oxygenated waters (salmonids, perch) or to succeed even in quite low DO (tench, carp).

An overall figure of DO for waters supporting salmonid fish was suggested by the European Inland Fisheries Advisory Commission: the annual 50-percentile[Note 21] concentration should be at least 9 mg/l but the annual 5-percentile could be as low as 5 mg/l. Corresponding figures for waters where moderately tolerant non-salmonid fish live were 5 and 2 mg/l respectively.

3.1.2 Temperature

Since fish *are* cold-blooded their rate of metabolism is largely dictated by the temperature of their surroundings. Water temperature therefore is a major controlling influence on the rates of embryonic development, growth, oxygen consumption, efficiency of food conversion and so on. The relationship is not necessarily simple however. Two-year old brown trout grow best at 7-9°C and 16-19°C, but not so well at intermediate temperatures. The reason for this unusual observation is the different ways in which temperature influences appetite and maintenance requirements. Salmonids have rather lower preferred temperatures than many other British species. Details are given in 3.2, but,

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[Note 19] Note the use of the word "degree" rather than the symbol "°". When referring to an increment in temperature we use the word; when we are discussing a particular temperature we use the symbol.

[Note 20] In this case we say that the temperature coefficient (Q_{10}), the increase in rate of a process (respiration for example) brought about by a 10 degree C increase in temperature, is 2.0. Values of the Q_{10} between 2 and 3 are quite common in biological and chemical processes.

[Note 21] An annual 50-percentile concentration is the central concentration in a ranked series of samples taken during one year. If there are 11 samples the observed 50-percentile is the sixth after ranking. This statistic can be interpolated from a plot of the individual ranked concentrations too. If there are 20 samples taken in a year the interpolated 5-percentile should be close to the lowest observed, and the 50-percentile should be somewhere near the values for the tenth and eleventh samples in the ranked series.

to give a guide, brown trout might be expected to spawn and the embryos to develop at 2-6°C while the normal range of these activities for roach would be 8-19°C.

Water temperature is fundamental to the physiology and behaviour of fish.

3.1.3 pH

A fish maintains its own internal pH, and its enzyme systems have evolved to be most successful at or around such pH values. Their ability to control pH is markedly greater than their very limited control of body temperature. The external pH has many influences on water chemistry (and *vice versa*) that may be very important to fish. Of course, extreme pH values can defeat the internal control mechanisms and kill fish. This aspect will be discussed in Section 5.

Freshwater fish in general can be expected to live successfully in a pH range of 6.5 to 9.0 (that is, from slightly acid to quite alkaline). Salmonids tend to be able to survive lower pH than non-salmonid fish but non-salmonids tend to be better able to cope with alkaline waters. (This arbitrary division of salmonids and non-salmonids into, respectively, sensitive and tolerant, will not apply to all cases.) Fish differ too throughout their life stages in their ability to tolerate extremes of acidity and alkalinity.

3.1.4 Suspended solids

Except for those suspended particles which either are food for very young salmonids or are otherwise important to the food chain[Note 22] of which salmonids are part, the fish themselves have no particular requirement for suspended solids. Indeed they can be harmful, as will be explained more fully later. However, concentrations of inert suspended solids up to 25 mg/l seem to have no harmful effects on fish, *provided that the solids remain in suspension*. Lower concentrations in the water column could lead to harmful effects if the solids were then to be deposited in quieter waters.

[Note 22] When we speak of *food chains* a picture of PLANT - HERBIVORE - CARNIVORE (grass - rabbit - fox, or algae - zooplankton - herring) comes to mind. This is too simple however. The energy in sunlight, trapped by plants, is indeed handed on, but generally in a complex way involving many interlinking chains, more properly called a *food web*. Suspended solids by absorbing light energy as the light passes through the water can therefore play a limiting role in all the subsequent events of the food web.

3.1.5 Cations

We can use cations[Note 15] to demonstrate the four numbered classes of substance listed at the beginning of Section 3.

(i)   Among the essential cations are calcium, magnesium, sodium and potassium (whose role has been described in 2.1.6), iron, manganese, molybdenum, copper, cobalt and zinc (see 2.1.8).

(ii)   Cadmium, lead and mercury seem to be non-essential and can be toxic at quite low concentrations (see 5.2).

(iii)   As well as the function of cobalt in relation to the utilisation of iron and copper in fish (2.1.8) Section 5.2 will demonstrate the importance of hardness (essentially the presence of calcium and magnesium) in modifying the toxicity of heavy metals.

(iv)   The *condition* of the surrounding medium in terms of pH and the presence of dissolved substances may greatly affect the needs of fish for cations and the ability of the fish to take up cations from the water.

This last point is less true of essential metals which have their origin in the diet of the fish. The gut wall may be quite resistant to the uptake of metals (as a defence mechanism perhaps, or just by chance). Fish faeces are very much richer in metals than their food is. Some metals, essential and non-essential, must get through the wall of the gut and into the tissues. There they may be used, stored for later use, stored out of harm's way or they may overwhelm the internal detoxifying/excretory processes and impair the enzyme systems, leading to stunting and death.

The major cationic component of the blood of a bony fish is sodium.

3.1.6 Anions

Just as sodium dominates the cations, chloride dominates the anions in fish blood[Note 23]. Bicarbonate and phosphate in total only equal about 10% of the chloride concentration. Sulphate is even less abundant. (Sulphur is another essential element; it is found in amino acids (the constituents of proteins) and many enzymes.)

3.2   The Water Quality Requirements of Each Life-cycle Stage

The various distinct life-cycle stages of a fish may have rather similar water quality requirements, but they are grouped in this section into what is hoped are logical units. These are **spawning**, to enable a discussion of what is needed for successful migration upstream to an appropriate site, the **intragravel stages**, egg-burial, embryonic development, hatching and egression from the redd, **fry and parr**, the juvenile stages leading, in the case of the migratory forms, to smolts, which may have to make a downstream migration through poor water quality conditions, a brief note on the **adults**, whether or not they are at sea, and finally the **returning adults**.

3.2.1 Spawning

To reach the spawning site the adults must have experienced adequate water quality conditions throughout their lives to that point.   In particular they required water of sufficient DO for them to move upstream, perhaps passing through estuaries, swimming over weirs or jumping obstacles - activities which demand far more than the basal metabolic oxygen requirements. Salmonids seem to exhibit many kinds of behaviour pattern in migrating to the spawning area. They may make a sustained effort and reach it in one steady journey, or they may move in stages, staying for many days between upstream movements.

Before this they must find the correct river or tributary. It is hard to imagine anything other than a chemical stimulus in the last phases of salmon migration. Oceanic gyres, temperature gradients and other major navigation marks are no longer present when the last decision - "Which tributary?" - has to be made. If chemical perception is important, so is anything that could upset the olfactory system of the fish. Tainting could mask the

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(Note 23)   Fish blood and fish urine contain the same range of substances but in very different proportions. A bony freshwater fish needs to retain its vital supply of sodium and chloride ions. The kidney achieves this by resorbing Na and Cl. Sulphate is not needed except at low concentration and so it passes out with the urine, but in far higher concentrations than in blood.

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sought-for taste/smell, or a pollutant could reduce the efficiency of the olfactory nerves. Such pollutants are known.

Once on the spawning bed the aggression of the cock fish imposes another metabolic cost. Poor quality water on top of all this natural stress could kill the fish before they have had a chance to breed.

Next, in order to spawn, the hen fish must find suitable gravel. If it's covered in silt she won't succeed, and it would be of little use anyway. This leads on to the next phase in the life-cycle.

3.2.2 Intra-gravel stages

The hen fish excavates 'egg pockets' in gravel - probably to a depth that is in proportion to her own length. She sheds eggs in the cavity, the male ejects milt over the eggs (sometimes with a prematurely fertile small male, which has never been to sea, sneaking into the egg pocket to fertilise the deepest lying eggs, or to eat them) and then the eggs are buried as the next egg pocket immediately upstream is excavated - and so on till the *redd* is completed.

Eggs of salmonids lie buried in the gravel for a long period. The water is very cold for much of this time and development is slow. Even so, the buried eggs have water quality requirements which must be met by the water percolating downward through the gravel from the river above. The water has two functions: to bring oxygen to the developing embryo within the egg (and later to the newly hatched alevins) and to carry away wastes which may have diffused out through the egg membrane.

In order for these functions to occur it is essential that the flow of *interstitial water* should not be unimpeded by silt, for example. The eggs in the gravel must be bathed in water containing plenty of oxygen. As oxygen diffuses in through the egg membrane, carbon dioxide, ammonia and other waste products diffuse out. They arise in embryonic development as stored food (yolk) is converted into complex tissues and organs.

The fish egg seems to vary in its response to different pollutants. Eggs are rather resistant to zinc compared with the early free-living stages but, in contrast, sensitive to ammonia. Perhaps the zinc doesn't penetrate the egg membrane. Ammonia does, because that is its normal route of exit from inside the egg. So it is possible that if a salmonid egg was in a flow of water already containing ammonia, and if there was too little difference between the concentrations of ammonia inside and outside the egg, then the metabolic waste ammonia from the embryo might not be able to get out as fast as it was produced.

The ammonia in the egg would therefore increase, and, if sufficient difference in concentration was still not developed, the ammonia would reach toxic levels, just as it would if the water had a higher concentration of ammonia than that inside the egg, in which case ammonia would enter the egg. The embryo would die.

The rate of development of the embryo and the time taken to hatch are mostly dependent on temperature, but a slight lack of oxygen can cause delayed hatching. It is outside the scope of this Blue Book to discuss the details; it is sufficient to note that the relationships between temperature and the onset of hatching have been extensively studied, and that trout and salmon need about 410 and 440 day-degrees C to hatch[Note 24]

Salmonid fry live for some days within the gravel after hatching. During this period they continue to feed off their stored yolk and they continue to require the same general quality of water as the eggs. However they seem to be rather more tolerant of ammonia and rather more sensitive to zinc.

3.2.3 Fry and parr

On emerging from the safety of the gravel the fry must expend energy to swim and to find their food. They can be particularly sensitive to stresses of many sorts at this stage, when they are using up the last of their yolk and beginning to hunt for food. In terms of water quality they simply need plenty of oxygen, not too much heat and an absence of pollutants, both for themselves and the organisms on which they feed.

3.2.4 Smolts

The same is true for salmon and sea trout smolts as their colouration and behaviour change and they begin to move downstream. There is generally more chance of fish encountering poorer quality water as the river nears the sea. The river is now increasingly under the influence of man's activities and the quality observed is an increment of all the inputs it has received upstream, minus the effects of the river's own ability to degrade pollutants.

It is also possible that the time of arrival of the smolts at the head of the estuary is quite critical in relation to estuarine water quality. Estuaries, like lakes (and UK rivers to

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[Note 24] *Day-degrees*: This is simply the temperature multiplied by the number of days that the temperature occurs. In a simple case of constant temperature 440 day-degrees C could occur if a temperature of 4°C lasted for 110 days, or if 8°C lasted for 55 days. Sometimes the relationship is a little more complicated: there can be a threshold temperature, below which no useful progress is made towards (for example) the development if an insect egg or larva towards its next stage.

a lesser extent), have marked seasonal patterns, superimposed, in the case of estuaries, on the tidal cycles. In the warmer seasons there can be periods when an estuary shows marked decreases in dissolved oxygen. These may not be due to the immediate past input of pollutants, but to the resuspension, the churning up, of oxygen-demanding silt which may have been deposited and have accumulated over many months. Thus if water quality progressively deteriorates as temperatures rise, a late smolt run may encounter far worse conditions than an earlier escapement. So if any change occurs in the nursery area over the preceding period which may slow down the rate of smoltification, such as increased shading due to afforestation or the release of colder, deeper water from a regulating reservoir, this can have far-reaching consequences for the smolts when they are distant from their nursery area.

Normally however the greatest physiological challenge for the smolts is the switch from fresh water to marine life. Salts which had to be retained in the body by special mechanisms in fresh water now surround the fish in abundance. The problems now are firstly to keep the blood dilute enough to carry out the functions of the tissues, against the concentration gradient caused by the sea being three times saltier than fish blood, and secondly to change to an entirely different form of nitrogen excretion.

As discussed above, ammonia is an extremely toxic substance, but when fish are in fresh water, waste nitrogen is converted into ammonia. It can only play this role effectively in fresh water because it is only here that there is sufficient outflow of water from the fish to carry the poison away in the excretory stream. In the sea the fish is faced with the reverse problem: there is no water to spare! In this case the excretory product is trimethylamine oxide[Note 25], a less toxic material which does not require a large flow of out-going water. The smolt may have to achieve this physiological switch in a very short period, and so may the adult on its return from the sea. Fish in the sea drink quite large volumes and then excrete the unwanted salts.

The critical organs for salt and water balance are the kidney and the gill. Any damage to these tissues may thus have serious consequences for the smolt as it enters the estuary.

[Note 25] Cartilaginous fish such as the shark not only convert waste nitrogen to urea, as mammals do, they also hold that urea in their bloodstream to build up the osmotic strength of their blood so that they do not have the problem of potential water loss to contend with.

3.2.5 Adults

The brown trout in inland waters and the sea trout and salmon at sea now feed and grow towards their mature size. Growth is, of course, especially rapid at sea.

In the oceans there is, as yet, little likelihood of severe pollution affecting salmonids, but they may be accumulating traces of man-made chemicals (see 5.2). When salmonids approach coastal waters they may encounter poorer quality water. For example cases are being reported of eutrophication (2.1.5) in the Baltic, the northern Adriatic and the Waddensee. The algal blooms which are forming can reduce the dissolved oxygen level at night to a point which is lethal to fish.

The requirement for marine and freshwater adults is obviously to avoid all of these harmful water quality characteristics and to find well-oxygenated waters teeming with food organisms!

3.2.6 Returning adults

Now we return to the problems mentioned in 3.2.1. The adults must find their natal river or tributary and must be stimulated to ascend by flow, chemistry, season or some other factor acting alone or in combination.

Oxygen, now and throughout the salmonid life-cycle is the single most important requirement for the fish, to enable it to utilise its food to release the energy it requires to respond to the stimuli essential for survival of the species.

4. CAUSES OF DETERIORATION IN WATER QUALITY

4.1 Introduction

Section 4 is going to describe the origins of pollutants, but first a definition of pollution is required. A generally accepted interpretation is:-

> The discharge by man, directly or indirectly, of substances or energy into the aquatic environment, the results of which are such as to cause hazards to human health, harm to living resources and to aquatic ecosystems, damage to amenities or interference with other legitimate uses of water.

It can be useful to classify pollutants in a number of arbitrary ways. For example, in Section 5 the classes are *physical*, *chemical* and *biological*. Here however the classes to

consider refer to the pattern of occurrence of the pollutant. We can contrast *diffuse* sources from *point* sources. Where pollutants enter a waterbody at some discrete point, as from an effluent discharge pipe, we call that a **point source**. Sewage works, storm sewers, industrial-waste outfalls or farm and factory yard drains are examples. When pollutants enter a watercourse at many smaller points, for instance in leachates from land (such as fertilizer or pesticide loss from farmland or forests), herbicide drainage from railway tracks and 'acid rain' from car exhausts or power stations we term these **diffuse sources**. These last two examples would be counted as point sources of atmospheric pollution and, subsequently, diffuse sources of terrestrial and aquatic pollution.

Point sources are much more easily treated than diffuse sources, which is why the strategy of removing sulphurous compounds at power stations by flue-gas desulphurisation (FGD), or oxides of nitrogen from power stations and car exhausts has to be a far more fundamental and effective solution to the acid rain problem than simply liming the soils affected, expedient though this may be. Figure 2 represents the two classes of pollution discussed above.

Another arbitrary but interesting classification of pollutants is based on the reason for their production. Pollution could occur because a previously stable use of land or water gives way to a new form of land use. Examples from *changing land use* might be the building of a motorway or the afforestation of a tract of moorland. Examples from *static land use* would be the general mixture of industrial and domestic wastes arising from an established urban community, or the pollution from an existing fish farm.

Section 4.2 divides the causes of freshwater pollution into uses of land. Some (effects of airfields on groundwater) may never affect salmon or trout, but they are included in an attempt at a complete picture. Section 4.3 gives a summary of similar information for estuaries. The pollutants themselves are described in Section 5. Routes to the receiving water are given for some wastes in Figure 3.

In reading Sections 4.2 to 5.2 it should be remembered that the degree of severity of any polluting activity will depend on the nature of the receiving water (for example some of the features shown in Fig. 1) and on broader factors such as climate. it has been said that as a result of global air pollution and the removal of major forests our European climate is tending towards greater variability with more frequent extremes. It certainly seems the case that in south west England summer base flows are often only half their previous values while winters have become wetter. These factors will influence the pollutant diluting and carrying capacity of waters.
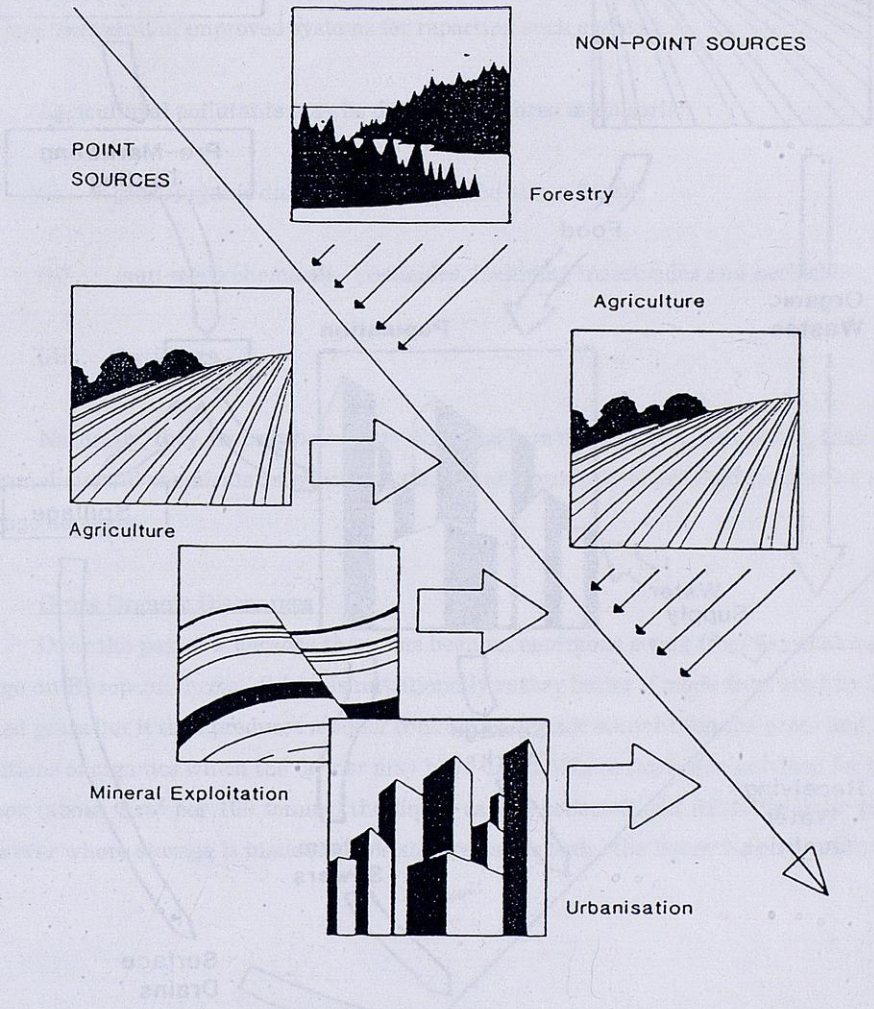
Figure 2 Sources and patterns of pollution of inland surface waters
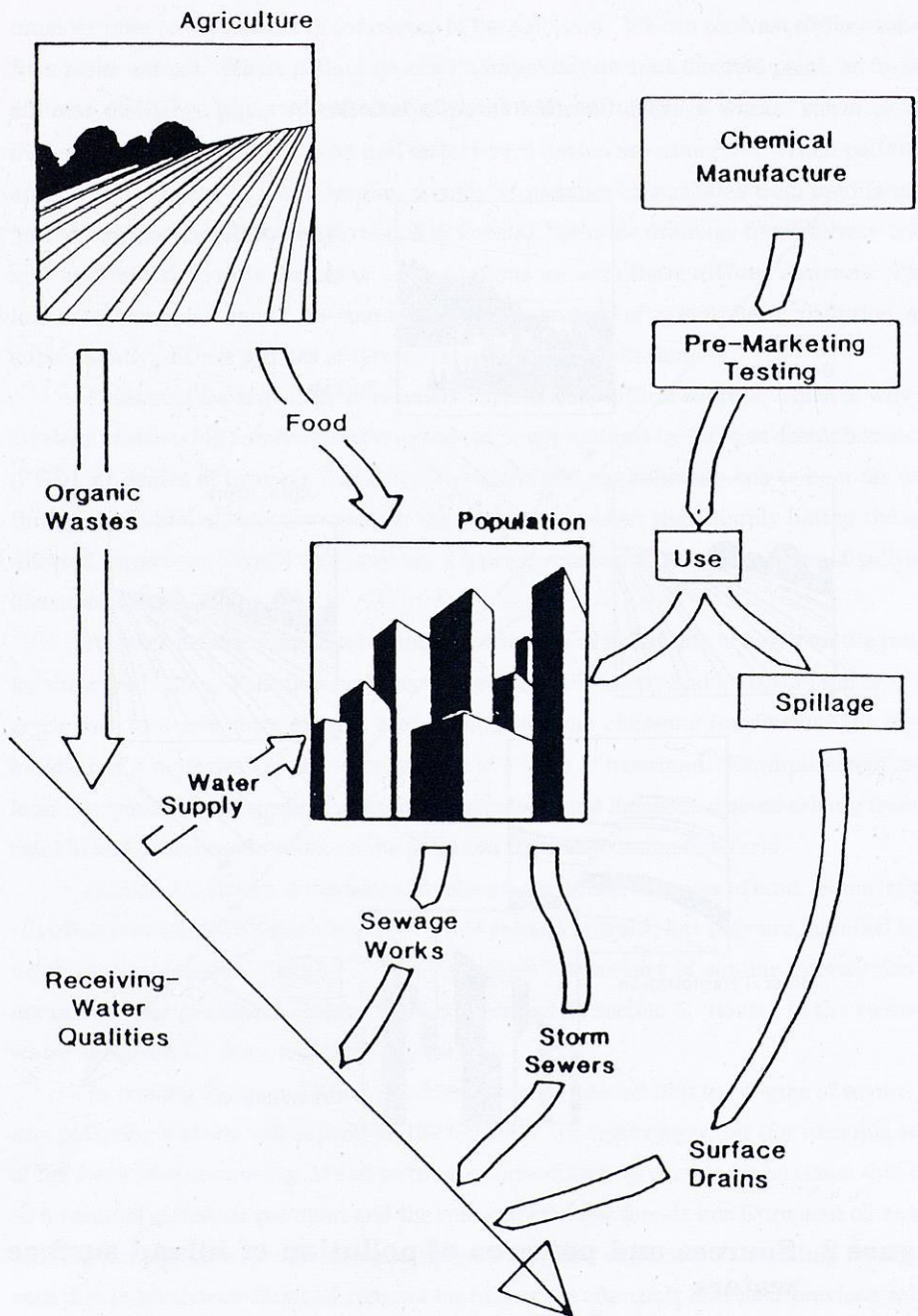
Figure 3 Possible pathways of a chemical to the receiving water

4.2   Causes of Pollution in Fresh Waters

4.2.1   Agriculture

It may seem a little unfair to start with an industry on which we all depend for our continued existence, but in recent years agriculture has been recognised as a major and increasing cause of pollution of fresh waters. This increase seems to have been genuine, and not just the result of improved systems for reporting such events.

Agricultural pollutants may be divided into three main sorts:

(i)   gross organic discharges - slurry and silage liquor;

(ii)   man-made chemicals - pesticides, including insecticides and herbicides;

(iii)   fertilizers.

Naturally, they are only *pollutants* when they are out of place. Otherwise, they are extremely useful chemicals on which the quality and quantity of our food production and storage depends.

(i)   <u>Gross Organic Discharges</u>

Over the past few decades there has been an enormous swing from hay-making to silage on European farms. *Silage* is nutritionally rather better if made from slightly less wilted grass but it then produces a liquor containing organic matter from the grass and the additions of organics which the farmer may have used. Where storage is provided for this *liquor* (about 1 m^3 per 100 tonnes) the liquor can be collected and fed to cattle or pigs. However where storage is inadequate or storage tanks leak - the liquor is very corrosive -

the liquid may reach a watercourse with devastating effect. The biochemical oxygen demand[Note 26] of this pollutant can be 90,000 mg/l. One litre of silage liquor would completed remove all the oxygen from 9,000 litres of clean, well-aerated water at 15°C. Such dilution can hardly ever be available in streams. Domestic sewage, with a BOD of about 300 mg/l, would only totally deoxygenate about 30 times its own volume of clean water under the same conditions; once treated, the resulting domestic sewage-treatment plant effluent only has a BOD of about 20 mg/l.

Slurry is the modern equivalent of farmyard manure. It is stored in tanks or lagoons until conditions are suitable for its utilisation on the land. Two problems are often seen: heavy rain after the slurry has been spread can result in the material being washed off the land and entering watercourses; lagoons or tanks may overflow or leak, or at worst, burst. It is important to maintain such structures and to separate clean rain water from foul drainage, so that the storage system is not overloaded. The effects are the same as with silage liquor but slurry does not have quite the same high BOD as silage. It can make up for this by its greater volume however. The effects are detailed in Section 6.

(ii)   Pesticides

For the foreseeable future, most farmers will continue to use various chemicals to achieve the necessary levels of production. Pesticides - insecticides, fungicides and herbicides, will be used in the field. The rules for handling these toxic chemicals in order to safeguard the farm worker and other non-target organisms(!) are quite clearly laid down in the publications of the Agricultural Development and Advisory Service. Unfortunately leaching, spray drift and the careless or accidental handling of pesticides can produce immediate, briefly delayed (months) or very long term problems to the aquatic environment. Containers buried many years before can corrode and lead to serious damage to fish stocks in future years. There are remedies, but they are expensive. Further facets of the effects of pesticides are given in 5.2.

[Note 26] Biochemical oxygen demand (BOD) is a measure of the amount of easily degradable organic matter in a sample of water. It is measured by determining how much oxygen is consumed by the sample over a five-day period at 20°C in the dark. A small volume of the sample is placed in a bottle, to which is added an inoculum, usually of sewage effluent. The effluent contains micro-organisms which, if they can degrade the organic matter in the sample, consume oxygen in so doing. Since the bottle is sealed at the start of the five days, no more oxygen can be used than is the bottle on Day 0. This often means that a sample such as a silage liquor has to be diluted considerably before the BOD test starts (or the oxygen would be entirely consumed in minutes). However, calculations relate the demand to a full litre of full-strength sample, as in 90,000 mg/l.

(iii) Fertilizers

As with pesticides, there will be a continuing need for fertilizers to maintain soil fertility. Nitrogen, phosphorus and potassium will be applied, supplemented where possible by slurry and sewage sludge. The inorganic nutrients may be washed off the soil surface by heavy rain or may seep down through the soil layers or 'horizons' towards the groundwater. Nitrogen is far more likely to do this than phosphorus because the latter element is strongly adsorbed by a wide variety of substances in soil and is thus likely to stick in the horizons near the surface. The effects of these nutrients, if they do get into surface waters, have already been touched on in Section 2.1.5 and will be discussed further in 5.2.

Incidentally, the fears that chlorine-based disinfectants used in dairy parlours might influence salmonid waters seem unfounded. Free chlorine (see 5.2.4) would be rapidly mopped up by any organic matter and rendered harmless.

4.2.2 Forestry

Since so much of our coniferous forest has been planted in the uplands[(Note 27)] where salmonid spawning and nursery areas abound, it is important to understand the possible consequences of forestry practice on streams, and to seek measures to avoid problems. A useful Forestry Commission Leaflet (No 78) has been prepared by Dr D H Mills on the management of forest streams. Updated guidelines are available from The Forestry Commission ('Forests and Water: Guidelines', ISBN 0 855 38 229 5) which cover the broader aspects of forest management and water.

The production stages that occur in forestry, all of which can cause environmental damage, are (i) afforestation, (ii) forest 'maintenance' and (iii) deforestation. Some of the harmful effects are common to all - such as the spillage of fuel or damage to spawning fords used by heavy vehicles - but those which are particular to each stage are briefly discussed below.

(i) Afforestation

Generally before ploughing or drainage can be carried out ready for planting the trees, a road system must be built. In all these operations there is a real risk of erosion, the nature of which will depend on the quality of the work and on the soil or rock. Solids may

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[(Note 27)] The commonly accepted definition of *uplands* at present is land over 800 ft (240 metres).

enter the streams, and if the furrows, drains and roads are not cut with great care erosion may continue for many years. The consequent silting up of the watercourses would damage spawning areas and aquatic insect life (see 5.1.2). Bridges, culverts and impoundments for fire-fighting can all impede the movement of fish, if not properly constructed.

Drainage not only has the potential for creating bad siltation of upland streams, it also alters the natural pattern of stream flow (the "hydrograph"). An undrained upland area of peaty soils acts rather like a sponge, absorbing winter rainfall and releasing it gradually during the summer. When the uplands are drained they release their winter rainfall rapidly (so rapidly that the receiving streams may then erode their banks and beds); in dry weather there may be no water left in the peat to provide the natural summer base flow.

To give the trees a good start weeds may be suppressed using herbicides. Fertilizer, usually phosphorus and potassium, may be added.

By the use of carefully designed planting patterns many problems can be lessened, otherwise some or all of the following section may apply.

(ii)   Forest Maintenance

During the ageing of the forest a number of management procedures may be needed. The trees may be thinned, to maintain the right balance between stunting and too rapid growth. (The latter gives timber with poor structural properties.) They may require more phosphorus after perhaps 10 years and of course any severe outbreak of insect pests may require the use of a pesticide. Both phosphorus and pesticide applications are carried out from the air at this stage. The principal problem with pesticides is probably related more to spillage than to approved patterns of use.

Without any other influence by man, forests as they grow cause three other problems - **shading**, **acidification** and **loss of water yield**. The first two of these can be kept to a low level if the trees are planted well back from the stream but the third is an almost inevitable consequence of the growth of trees. Lost water yield results from the relatively high rate of evapotranspiration[Note 28] from trees compared with the previous vegetation. For every 10% of a catchment area which is afforested roughly 2% of the water yield is lost. This may not sound much, but when thinking of land three-quarters afforested and suffering low

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[Note 28]   The term *evapotranspiration* is a recognition of the fact that water which leaves a tree originates both from within the tissues of the tree (transpiration) and as simple evaporation of water which has fallen onto the surface of the tree). (The extent of evapotranspiration may be guessed when one sees a mist drifting up from a forest during humid conditions.)

summer base flows it could be critical for fisheries as well as water supply, hydro-electric power and other downstream uses.

Shading of a stream is desirable to some extent but beyond this it limits primary production and therefore the whole food web[Note 22]. Springtime rises in temperature may be delayed, reducing the period of the growing season. A long length of complete shade is almost entirely unproductive.

Any tree is more or less capable of acidifying the soils on which it grows. Much depends on the soils, what their buffering capacity is[Note 7]. Just as a fish maintains its pH by controlling its ionic balance, so a tree, preferentially taking in positively charged calcium, and other, ions through the roots, is prevented from becoming positively charged itself by excreting hydrogen ions (ie acids) from its crown. These acids are washed down the tree during rainfall, together with any atmospheric pollutants the tree may have *scoured* from the atmosphere since the last rain. In addition to this 'dry deposition', trees with their finely divided leaves and twigs collect mist droplets, concentrating the aerial pollutants and directing them to the soil. The soil water may move quickly to the stream or may percolate more slowly. If the former, there is a possibility that acid pulses will be apparent in the stream. Providing a buffer zone between the tree and the stream improves the chances of the acid being buffered by the soil, if it has sufficient buffering capacity. Calcareous soils like chalk obviously have an enormous buffering potential but unfortunately most of the intensive forestry in Britain is on the western and northern rocks, which are hard and non-calcareous.

Acid waters in soils have another important and serious effect: they can dissolve aluminium. The consequences of this are dealt with in 5.2.

(iii)   Deforestation

This third stage in the life of a forest may be accompanied by problems similar to those of afforestation - road usage leading to erosion, and solids in watercourses. In addition the *brash*, the "lop and top", will possibly be left, to enter and dam up streams. Nutrients may leach out of this material but the consequences for fish communities are not considered serious.

4.2.3 Industry

The subject of pollution caused by industrial activity has occupied entire books. When raw materials (minerals, wood or food) are gathered, refined and used they can cause pollution. The details of this enormous subject are summarised in Appendix A, which includes metallic, acidic and solids contamination from mineral exploitation and heavy industry. The range of pollutants which can also arise from the chemical industry, textiles, timber products and the food industry is also mentioned.

Industrial materials have to be properly processed for them to perform the functions we require of them, but there may be consequences for the environment, for surface waters in general and, to a smaller extent, to salmon and trout streams in particular.

4.2.4 Domestic wastes

Two sorts of sewerage system may be found in the British Isles, and in addition houses may not be connected to a sewer but may use septic tanks. The two sorts are 'separate' and 'combined'. In separate systems the foul sewage is carried separately from surface water (street) drainage. In a combined system the two types of waste water use the same sewers. Urban rivers are often in a poor state, not because of the quality of their dry-weather flow but as a consequence of the intermittent flows of storm water they receive when the flow exceeds the carrying capacity of the sewer. In combined sewerage systems the storm water contains raw sewage.

In dry weather and moderate rainfall all the sewage reaches the sewage treatment works. Here it receives treatment by *grit removal*, *sedimentation* (producing a *sludge* which is *digested* to reduce its volume considerably and its water content a little), *biological oxidation* of the liquid *settled sewage* in percolating filters or activated sludge plants, followed by further sedimentation (the sludge being mostly sent back to the primary sedimentation tank or (a little) used as an inoculum in the activated sludge process), followed finally by tertiary treatment and/or discharge of the effluent. No matter what the method of treatment, the final result should be a clear liquid effluent and a digested sludge. The sludge may be useful in agriculture, depending on the contribution of industrial wastes to the sewage works. Domestic sewage sludge should present no problems in this respect because it contains few heavy metals in any significant concentration and should not be toxic to plants, or "phytotoxic".

The 'clear liquid' sewage works effluent contains a little ammonia, nitrite and nitrate, degradable organics (BOD), other more resistant organics and suspended solids.

Efficiency varies with season but much of the organic wastes in sewage is 'burnt off' as carbon dioxide by the organisms of the biological oxidation plant - bacteria, protozoa, fungi and macro-organisms such as flies and worms.

4.2.5 Power generation

Four principal problems may be caused for fish by the generation of electricity. These are barriers to fish movement from dams used in hydro-electric schemes, entrainment in the flow through the turbines or cooling systems, heated effluents from cooling circuits and acidification of waters from the combustion of fossil fuels. The first three of these have immediate effects in the proximity of the power station. The last may cause problems thousands of kilometres from the sources of contamination. Only the last is covered further in this section.

Coals and oils contain many other elements than carbon, hydrogen and oxygen. Sulphur, nitrogen and chlorine, but especially sulphur, give rise to particular problems for the environment. The sulphur is oxidised to sulphur dioxide, SO_2, in the power station furnaces and passes up the tall stacks to be dispersed in the atmosphere. Unfortunately the sheer mass of SO_2 produced and the existence in Europe and North America of areas of land vulnerable to acidification defeat this attempt to dilute the gas to insignificant levels.

The problem is created because SO_2 is oxidised to SO in the atmosphere and dissolves in water to form sulphuric acid. Secondly, coniferous trees 'scour' such substances from the atmosphere and thus concentrate them again. Thirdly, the upland soils receiving the most rain, and therefore the most acidity, are often non-calcareous and have already lost much of what little buffering capacity they had. They still retain some however, in the form of aluminium, but sadly, although aluminium does increase the alkalinity a little, it is an extremely toxic metal under relatively acidic conditions.

Other features of the uplands conspire to increase the toxicity of the waters draining from them. The first is natural - *snow* - and the second artificial - *upland management*.

Snow may accumulate acidity which is then released all at once during the spring thaw. (Another possibility is that what we observe in streams at this time is the release of soil water expressed as the snow melts into the upper soil, the soil water having gradually accumulated aluminium in solution during the period of snow cover. This is still a matter for debate: both theories may be true.)

Upland management may include drainage for forestry (4.2.2). The acid rain then has less contact time with the alkaline constituents, cations, in the soil - less chance for a

reduction in acidity. There is far less burning of heather or liming of upland pastures now. Both these activities provided cations available for buffering.

The nett result of all these factors is the existence in many upland areas of streams liable to episodes of acidity and high aluminium.

The primary culprit in this sub-section has been sulphur dioxide, but nitrogen dioxide is equally capable of causing enhanced acidity, and this is touched on in the next sub-section.

4.2.6 Transport

(a) Road

Various oxides of nitrogen are emitted from petrol engines and so of course is lead. Motorway drains and urban streets accumulate heavy metals from vehicles[Note 29]. These may find their way directly, indirectly, treated or untreated into streams.

An enormous variety of chemicals is carried by road; any of these could enter watercourses as a result of road traffic accidents. There are procedures to be followed by fire brigades in dealing with such incidents, but inevitably there will be occasions when material from the road surface finds its way into streams.

(b) Rail

It has been correctly said that railway tracks are the longest sewage percolating filters in the country, but the disposal of passengers' sewage is so diffuse as to produce no recognisable problem.

What matters more, to the water supply industry, results from the need for the permanent way to be kept free of weeds. Herbicide-spraying trains are regularly used, and this could be a source of pollution of track-side ditches and streams.

(c) Air

It may seem unlikely, but airfields can be a source of pollution for ground and surface waters. De-icing chemicals, fuel and de-greasing agents may all pose problems.

Transport by water is more conveniently dealt with under Recreation, below.

[Note 29] It has been calculated from drain samples that 4 kg of lead, 8 kg of zinc and 126 kg of oils run off each kilometre of motorway in a year.

4.2.7 Recreation

Boats may damage habitats by leakage of fuel, the use of certain antifouling paints (although tri-organo tins are now banned), the discharge of sewage (normally required to be retained and pumped out at purpose-built reception points), and turbulence. It isn't just the large motor boats which can stir up sediment or uproot vegetation: canoes can also cause such damage, though mostly in shallow silty streams.

Anglers too are not faultless. The need for legislation to enforce the transfer from lead to alternative weights, and public complaints about litter and trampled vegetation emphasise the point. However, to the salmon and trout the danger from anglers is obvious ... and non-polluting!

There is another danger: the incautious introduction of alien species, and even the introduction of native species of an inappropriate genetic strain; but this is stretching the limits of the term 'water pollution' too far.

4.2.8 Fish farming

The intensive production of fish for the table or re-stocking can be a major source of pollution for rivers inhabited by salmonids. All fish farms produce the same kinds of contaminants, but their polluting effects depend on the nature of the water receiving these waste products, particularly whether the receiving water is standing or running.

Raceways and ponds often discharge into running waters; cage-rearing is of necessity carried out in still or slow-moving waters.

Fundamentally, the pollutants arising from fish farms are the result of the quality of food fed to the fish, and the ability of the fish to consume and utilise it. In addition there may be antibiotics and disinfectant chemicals which appear from time to time in the effluent or in the environs of the cage.

The principal contaminants are suspended solids, ammonia or other forms of nitrogen, and phosphorus. These appear in relation to the amount of food fed. As an approximation, 1.5-1.7 tonnes of dry food produce about 1.0 tonnes of marketable fish. They also give about 15 kg of waste phosphorus (see 2.1.5) and 500 kg of waste solids. Fish farming is particularly likely to affect salmonid waters because (a) it is an industry which needs the equivalent of salmonid waters in order to supply the needs of the salmonids on the farm and (b) there is very little treatment of the farm wastes before they are discharged. There is however a growing awareness among fish-farmers of the need to discharge *treated* effluent, and a growing simple technology to enable them to do so.

Other problems are more intransigent. In order to treat or prevent diseases the farmer can use a variety of therapeutic or prophylactic chemicals, including antibiotics. Some antibiotic is lost to the environment, so bacteria in the receiving water may be given the chance of developing resistance to the antibiotic. Resistant bacteria pose a threat to other fish farms and to wild populations because the fishes own immune system may be stretched to cope with the infection or because weakened farm fish may 'culture' other diseases against which the wild populations may have no defence.

Disease controls are aimed at minimising the import and spread of infectious organisms, including parasites. Where infected stock have been introduced there are cases of parasites spreading to native stocks.

Two other problems are relevant to the protection of native salmon and trout: smolts or other young stages may be drawn into fish farms and large farmed fish may occasionally escape (and are said then to wreak havoc among smaller native fish).

4.2.9 Conclusions to Section 4.2

Clearly there are features in common in the wastes of widely varying industries and human activities. Some of the routes they may take to reach the environment have been indicated in Figure 3. The wastes include plant nutrients, simple and complex organics, acids and alkalis, heavy metals and other organics.

Having described the sources of pollution in Section 4.2, their effects will be described in Section 5, following the short note below on pollution in estuaries.

4.3 Causes of Pollution in Estuaries

There is nothing unique about the causes of pollution in estuaries, although heavy engineering has tended to develop around such examples as the Clyde, Mersey, Thames, Humber, Tees and Tyne. What does affect any consideration of estuarine pollution from the point of view of salmonids is the way in which conservative or poorly degraded pollutants may be retained by estuaries for many tidal cycles (70 days in the Thames for example under common conditions of flow).

A consequence of this may be that oxygen-demanding substances have an opportunity to express that demand to the full, so that, for all their immense volume, estuaries may exhibit low DO, possibly in one block of water which moves up and down the estuary with the tide.

As far as the migrating salmonid is concerned the polluted estuary represents a constantly moving set of environmental conditions and challenges which must be swum through at least twice in the life-cycle.

5.   EFFECTS OF POLLUTION ON FISH

Among the many books on this subject the publications of the European Inland Fisheries Advisory Commission (EIFAC) contain the most comprehensive reviews of given pollutants (see Bibliography, Section 8). Here, a synopsis of effects of pollution on fish and their food organisms is presented, based on the arbitrary division of pollutants already proposed, into *physical*, *chemical* and *biological*.

Where possible, an indication will be given of the toxicological mechanism involved in the effect, although it must be pointed out that this is frequently unknown. The effects of pollutants on fish may be due to superficial damage (particularly to the gill membrane) or to more deep-seated or 'systemic' damage. This difference may be far more to do with the concentration than the type of pollutant. We rarely know the effective *dose* of poison (the actual mass of poison required within the body to bring about a given effect). Instead we are able to define the ambient concentration necessary to cause a given effect in a given period of exposure. Table 1 lists examples of the pollutants to be discussed below.

Table 1   A Classification of Pollutants

| Physical | Chemical | | Biological |
	Inorganic	Organic	
Heat	Acids	Surfactants	Pathogens
Inert solids	Alkalis	Gross organic discharges	Parasites
- coal	Ammonia	- silage	Introduces species
- china clay etc	Chlorine	- slurry	
Oils	Cyanides	- sewage	
Radioactivity	Metals	Oils	
	Nitrates	Pesticides	
	Nitrites	Phenols	
	Phosphates		
	Sulphides		

5.1 Physical Pollution

5.1.1 Heat

All the biological processes in the aquatic environment have optimal temperatures or ranges of temperatures, outside which either a process may slow down and cease or may be severely damaged. heat from cooling circuits in power stations and other industries may increase water temperatures, although in winter this is unlikely to lead to any severe stress on the aquatic community. It may be the rate of change of temperature rather than any particular temperature which causes the stressful effects observed. The European Council Directive "on the quality of fresh waters needing protection or improvement in order to support fish life"[Note 30] recognised this by setting the following mandatory maxima on salmonid waters.

- general:	21.5°C
- spawning period:	10°C
- at edge of mixing zone down-stream of a thermal discharge:	increase of 1.5 degrees C[Note 19]

However, all these limits could be exceeded for 2% of the time. Although brown trout may be slowly acclimatised to 20°C they are normally then killed by constant exposure to 26-27°C.

5.1.2 Insert suspended solids

Solids with no discernible chemical activity may nevertheless have various deleterious effects on the environment. In addition to smothering spawning beds they can destroy the habitat of those invertebrates requiring a stony substrate, they can cut down the penetration of light to a point where plants can no longer live in the stream, and they can abrade or clog delicate membranes. For the gills of fish they present both these last problems. It takes a high concentration of solid wastes to clog a fish gill and cause asphyxiation, but only a little to cause abrasions and thus permit the possibility of secondary problems - infections. In addition, solids and other irritant materials may cause fish to secrete excessive amounts of mucus, to the point where the efficiency of gaseous- and ionic-exchange is severely impaired.

[Note 30] Where a river naturally exceeds the limits set out in the Directive a Member State may choose to seek derogation because it is "unable to control certain natural circumstances".

If the light is entirely excluded from a stream bed, as was the case in the china clay streams only a decade or so ago, trout may still survive in the absence of stream invertebrates by feeding on material which does not originate in the stream, for example insects alighting on the water surface. Naturally they will not grow as well as trout with a better food supply or where their ability to see their food is not so hampered.

The EC Directive sets a guideline maximum of 25 mg/l suspended solids.

As well as damaging fisheries, solids may be beneficial if metals or dangerous organics are adsorbed[Note 31] on them or bacteria grow on them, as they help a river to recover from the effects of pollution (see 6).

5.1.3 Radioactivity

There is no lower threshold for the production of cancers due to radioactivity but it is difficult to assign any particular carcinogenic agent to the observed incidents of malignant tumours in fish.

5.1.4 Oils

Oils have both physical and chemical effects (see 5.2.13). Physically they smother habitats and it may take a long time for the heavier fractions in an oil spill to disappear from a stream bed. In special circumstances they can benefit a stream: oils and grease in motorway drains soak up and lock away pollutants.

As far as the EC Directive is concerned it is easier not to give any maximum concentrations for petroleum hydrocarbons but to state that they must not form visible films, taint the fish or produce harmful effects in fish.

Among these harmful effects might be the prevention of gaseous exchange at the water surface, leading to reduced dissolved oxygen in the underlying water.

5.2 Chemical Pollutants

Table 1 shows that, for convenience, 'chemicals' has been divided into 'organics' and 'inorganics'. Within these sub-divisions the pollutants are taken alphabetically. Inorganics are dealt with first, then organics, and finally some general points about chemical pollutants.

[Note 31] We distinguish <u>adsorption</u>, in which a substance is taken up onto the surface of a solid, from <u>absorption</u>, where a substance is taken inside.

5.2.1 Acids

Mineral acids, as distinct from organic acids, may harm the aquatic environment directly, as for example by disrupting the important exchange of substances at the gill and 'acidifying' fish blood. Indirectly they may dissolve carbonates to the extent that toxic concentrations of carbon dioxide are liberated or may leach metals from deposits until they too are toxic. The situation is complex, needless to say, and water at a given low pH (acidity) will vary in toxicity depending on other factors. Carbon dioxide tends to increase toxicity; calcium tends to decrease it. In upland waters the concentration and form of dissolved aluminium may be an important factor in toxicity due to 'acidity'. The gill is the vulnerable organ, as so often, and extreme low pH may cause the fish to lose vital cations such as sodium *via* this route.

Invertebrates and fish vary in their sensitivity to low pH. Intra-specific differences may also have developed. During an acidic episode the effects of acidity are not necessarily irreversible. If a salmonid is removed from what would be a lethally acidic environment, even if the fish has been poisoned to the extent of losing equilibrium, it will generally recover when placed in a circum-neutral solution.

The EC Directive specifies the range pH 6-9 as that required by salmonid fish.

5.2.2 Alkalis

Problems from high pH discharges do not often seem to occur but certain pollutants, ammonia in particular, are made very much more toxic in slightly alkaline waters than in slightly acidic waters.

5.2.3 Ammonia

When ammonia dissolves in water it can react with water to give a mixture of the original ammonia (NH_3) and a new form, the ammonium ion (NH_4^+). The mixture is held in balance but a shift in pH can shift the proportions of each type[Note 32].

[Note 32] The equation describing the balance is:

$$NH_3 + (H^+OH^-) \rightleftharpoons NH_4^+ + OH^-$$
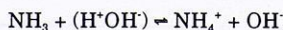
If the water is acidic (excess hydrogen ions, H^+) the equation is driven to the right. In alkaline (high pH) waters the balance moves in favour of unionized ammonia NH_3.

The toxicity of ammonia is due to the unionized form NH_3 and not to the ionized ammonium ion NH_4^+. Unionized ammonia is very rare at pH 7, only 0.19% being NH_3 at 10°C. At pH 8 ten times this percentage is NH_3, so water containing ammonia and ammonium will be ten times more toxic at pH 8 than in neutral water.

At pH values higher than 8.0 ammonia should have become even more toxic, but the late Dick Lloyd in the early 1960s found that it didn't. The explanation for his correct observation has more recently come to light: a fish can control the pH of the water passing over its gills. Carbon dioxide from the respiratory processes in the fish should react with water to form carbonic acid (2.1.3), which would tend to reduce the pH in the water bathing the fish gill, but the speed of reaction was calculated to be far too low to achieve the desired result in time: the water would already have left the gill chamber and been replaced by fresh water of high pH, making the ammonia toxic. The fascinating explanation is that trout can secrete an enzyme (carbonic anhydrase, 2.1.8) which speeds up the reaction (the principal function of enzymes is this acceleration process) and allows the fish to limit the pH around its gills to 8.0 or less.

The EC Directive specifies a mandatory maximum value for unionized ammonia of 25 µg/l (that is 25 parts of ammonia per thousand million of water, or 25 millionths of a gram per litre) with a guideline of 5 µg/l. Work at the Water Research Centre suggests that for rainbow trout eggs the former value may not be low enough (see 3.2.2). Conversely, later stages of the life-cycle may be able to adapt to ammonia, in other words to gain tolerance. In addition the mobile stages may avoid unsatisfactory conditions if a refuge of clean water is available. There is still much to be learned about ammonia toxicity and it remains an important pollutant.

5.2.4 Chlorine

The alphabetic arrangement of this sub-section has brought together three substances - ammonia, chlorine and cyanide - whose toxicity is dependent on pH. For chlorine the toxic species is not chlorine, Cl_2, but hypochlorous acid, HOCl. This acid is proportionately more abundant at low pH, so that it is almost absent at pH 9 (alkaline conditions) but at pH 7 it makes up more than 60% of the mix. Chlorine itself doesn't exist in aqueous solution for long enough to make its presence felt.

Fish can detect chlorine and move to try to avoid it.

When chlorine and phenols occur together they react to form chlorophenols which human taste buds can detect at 1 µg/l (one part in one thousand million). Chlorophenols are toxic too.

When chlorine and ammonia occur together they too react, to give a family of compounds called *chloramines*[Note 33]. The mixtures still contain HOCl and this is probably the cause of the toxicity of chloramines. (They are used as swimming pool disinfectants.) Chlorine tends to be 'mopped up' by any organic matter in the water as it acts as a strong oxidising agent (see note at end of 4.2.1).

In the EC Directive the mandatory maximum for salmonid waters is 5 µg/l as HOCl.

5.2.5 Cyanides

With cyanides too, the toxic species is the unionized molecule, HCN, rather than the cyanide ion, CN^-. This is not a coincidence; unionized molecules can pass more easily through the gill membrane. HCN, like HOCl but in contrast to NH_3, is favoured at low pH values. Cyanide acts by inhibiting the action of many vital enzymes.

For salmonids, a concentration of around 4 µg/l as HCN is lethal. There is no limit value for cyanide in the EC Directive.

5.2.6 Metals

Among the heavy metals currently recognised as toxic to fish are aluminium, cadmium, chromium, copper, iron, lead, mercury, nickel and zinc. Some of these can only express their toxicity under unusual conditions. For example, lead is so insoluble that it can only reach toxic levels in very soft waters; similarly iron will not remain in solution unless waters are highly acidic. Of course iron, precipitating out on the stream bed as ochre, can have devastating effects on stream life by smothering habitats.

As a general rule, the toxicity of heavy metals is lower in hard water than in soft water.

Other general points concerning metals and notes specific to each of the metals mentioned above are given in Appendix B. The notes include details of the standards set to protect fish populations from the effects of metals.

[Note 33] monochloramine, NH_2Cl; dichloramine, $NHCl_2$; trichloramine, NCl_3. The more highly substituted derivatives are favoured by (i) more acidic conditions and (ii) a greater proportion of chlorine in the mixture.

5.2.7 Nitrates

Although nitrates may be considered as pollutants, contributing to eutrophication, and toxic metals may be present in water as their nitrate salts, the anion NO_3 has no measurable toxicity *per se* at any realistic concentration. It may however be reduced to nitrite, NO_2, (see 5.2.8) to give problems.

Eutrophication can lead to harmful effects for fish - widely fluctuating levels of dissolved oxygen and pH and, at worst, the production, by blue-green algae, of *toxins*[Note 34]. Toxins from algae are among the most toxic poisons known.

5.2.8 Nitrites

Unlike nitrates, nitrites are very toxic to fish. The toxic species is the nitrite ion (NO_2^-). This is encouraged to form in alkaline waters. The presence of chloride strongly alleviates the toxic effects of nitrite.

The EC Directive level is 10 µg/l as NO_2 (about 3 µg/l as NO_2- N) for all waters. This seems excessively stringent, but was prepared without the benefit of the EIFAC study[Note 35].

Having now mentioned all but one of the principal components of the nitrogen cycle it might be appropriate to re-state the relationships of the inorganic forms, and at the same time discuss the toxic mechanisms of nitrite.

Ammonia, NH_3, leaving a sewage works, will normally be oxidised progressively to nitrite, NO_2 (by the bacterium *Nitrosomonas*) and then to nitrate, NO_3, by *Nitrobacter*. This process is termed *nitrification*. If anaerobic conditions occur due to excessive oxygen demand, the nitrate may be reduced to free nitrogen, N_2, again by bacteria, in the process known as *denitrification*.

Nitrite in the gut of a human or the gill chamber of a fish can pass into the bloodstream. In blood, nitrite reacts with the ferrous iron (Fe^{++}) in haemoglobin, oxidising it to ferric iron (Fe^{+++}) and thus creating *methaemoglobin*. This compound cannot transport oxygen and so the fish suffers from anaemia.

[Note 34] *Toxins* is a term which should only be used to describe those poisons derived from living organisms - atropine from deadly nightshade for example. Toxins are usually albuminoid substances of high molecular weight. Any poison can be called a *toxicant* however.

[Note 35] The greatest benefit (for rainbow trout) is seen where there is 17 times more chloride present than nitrite-nitrogen, by weight. So in this case the EIFAC standards propose five different nitrite levels for five chloride levels. They range from average values of 10 µg/l nitrite-N where there is only 1 mg/l chloride present to 150 µg/l NO_2-N in waters of 40 mg/l chloride. The 95-percentiles suggested are three times greater in each case.

5.2.9 Phosphates

Although elemental phosphorus is exceptionally toxic, causing *haemolysis* (breakdown of haemoglobin), phosphates, the common form of phosphorus encountered in fresh waters, only affect fish *via* the process of eutrophication, which has already been sufficiently described (2.1.5, 5.2.7).

The EC Directive suggests a limit of 0.2 mg/l as PO_4 for salmonid streams and provides an equation to calculate a phosphate value for lakes, in order to reduce eutrophication.

5.2.10 Sulphides

It must be obvious from the discussions on acid rain and leaching from spoil tips that sulphides are of great environmental significance. These cases have concerned the oxidation of sulphides to give acid solutions. In fact it is hydrogen sulphide, H_2S, which is the toxic species.

When metals in the mud of estuaries are mentioned it should be noted that these are almost always present as the sulphides. H_2S affects the same important enzyme as cyanide - *cytochrome oxidase* - but even more strongly. It occurs as a transient pollutant in urban streams when a storm first flushes out accumulated sulphide from the sewer. Anaerobic bacteria reduce sulphate to sulphide once any nitrate has been reduced.

No standards for sulphide have been written for freshwater fish. Probably the safest standard would be to require a total absence of H_2S.

II   ORGANIC CHEMICALS

Hundreds of thousands of organic chemicals are known, and many more are produced each year so that it would be quite impossible to give a proper account of all their known toxic actions and concentrations. Instead, a few general groupings of organic chemicals are described - detergents, gross organic discharges, oils, pesticides and phenols - in order to discuss some general principles of relevance to salmon and trout. In addition a short note is included on the recently described issue of 'environmental oestrogens'.

Figure 4 shows the fate of a chemical, through the stage of its pre-marketing trials to its marketing and subsequent release to the environment, either directly or *via* a sewage treatment works. Before the residue ends up in a *compartment* (or several compartments) of the environment much may happen to it, depending on its own characteristics and the

Fate and pathways of a chemical

Pre-manufacturing tests
physico-chemical
toxicological
ecotoxicological
Manufacture
Pre-marketing **Notification**
to a Competent Authority
Use
Release to environment

Direct   ADSORPTION
DEGRADATION
(ABIOTIC, BIOTIC)
DILUTION, DISPERSION
VOLATILISATION   Sewage
treatment
works   Indirect

ENVIRONMENT

AIR

SOIL

WATER
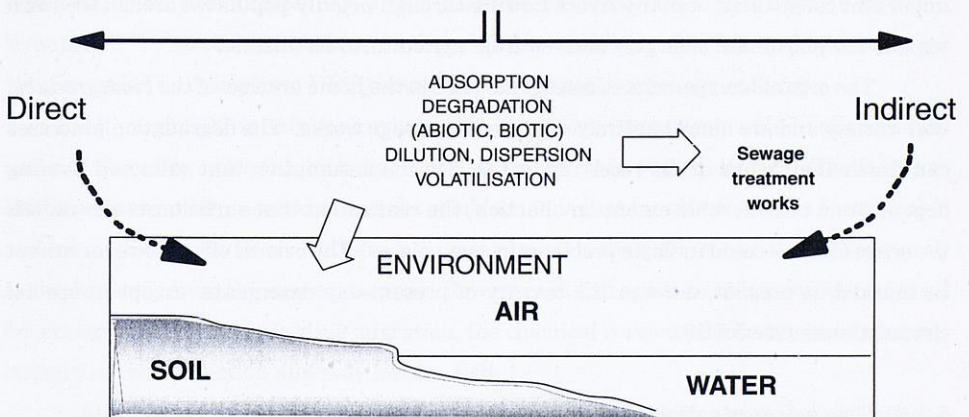
Figure 4   Possible events in the life of a chemical.

The proper use of degradable pesticides should not give rise to problems to fish. It is only when an accident occurs or containers of persistent chemicals are incorrectly disposed of that effects may be seen. These effects may be delayed for many years, during which, for example, buried containers are gradually corroding to the point where they finally start to leak.

5.2.15 Phenols

When the production of coal gas was still widespread, gas works were the source of many substances toxic to fish and aquatic life generally. Among these substances, phenols (phenol, cresols, xylenols) were common. Nowadays phenols are still used in industry and we can illustrate a particular point of more general relevance using them: phenols are more toxic at lower temperatures.

The reason for this is that phenols are examples of substances which fish can detoxify. The detoxification process is metabolic and its rate is therefore a function of the ambient temperature. The entry of the chemical is more or less independent of temperature (and phenol enters easily, for example through our skin). So in warm water phenol may be detoxified and excreted as fast as it enters the fish (up to a certain threshold of course). In colder water the phenol tends to accumulate in the tissues and the symptoms of poisoning begin to occur. Fish may become hyperactive and very often lose control of their pigmentation just before death.

The EC Directive only states that phenolic substances should not taint fish flesh but there is an EIFAC recommendation for protecting fish[Note 37].

5.2.16 Xenobiotic oestrogens

During the early 1990s a number of workers around the world reported an increasing incidence of reproductive disorders among wildlife (including fish, reptiles and birds). At the same time, a variety of problems seemed to be on the increase in human reproduction and in various forms of cancer. A programme of research was begun by the Department of the Environment and the Ministry of Agriculture, Fisheries and Food in the UK on the possible effects on reproduction in fish of something contained in domestic sewage effluents. Observations on young male rainbow trout held in undiluted effluent demonstrated that

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[Note 37] The EIFAC recommendation is that to ensure the long-term survival of salmonids the concentration of all monohydric phenols should not exceed 1 mg/l, or half this level if one particular xylenol is present *or where temperatures are lower than 5 °C.*

these fish were producing the yolk precursor protein *vitellogenin* at enormously elevated concentrations. A xenobiotic chemical or chemicals was possibly responsible, but so also was human oestrogen, excreted by women. (Xenobiotic means foreign to (new to) nature - man-made. Oestrogens are hormones responsible for a variety of functions in reproduction.) At the time of writing (May 1996) the situation is still unclear. Some rivers in the areas of textile industry may be carrying sufficient of one group of chemicals, the alkyl phenols, to produce the observed effects, but in other rivers, for example in less industrial areas, this explanation may not suffice. Water as it moves downstream from the effluent discharge and also when it is stored in reservoirs loses its oestrogenic potency. The significance for wild salmonids is also unclear. It is possible that there could be an impact if salmonid nursery areas occur downstream of industrial discharges or domestic sewage works, but whether the effects would be confined only to freshwater stages (with migratory forms 'recovering' at sea) or whether any of the observed effects would carry through to endanger long-term success of a fish population is a matter purely for speculation at this stage.

III   GENERAL POINTS ON CHEMICAL POLLUTION

In addition to the specific points made about such aspects as solubility in fat, the effect of hardness on metal toxicity or of pH on chemical speciation, it is appropriate to mention the effects of oxygen levels and salinity on toxicity and the possible inter-relationships of mixtures of poisons.

When a fish encounters water of relatively low dissolved oxygen it responds by pumping more water through its gill chamber. This compensates, more or less, for the lack of DO but brings the gills into increased contact with any pollutants in the water. Since the gill is the most important point of entry of poisons, the lower the DO the shorter the period before the fish succumbs. Also, lower concentrations of a wide variety of poisons are effective at lower DO than in fully air-saturated water. The effect is such that only about 70% of the normal lethal concentration is needed to kill fish at a DO of 60% of full saturation.

Not many studies have been made of the influence of salinity on toxicity, but generally the picture is of toxicity increasing as salinity approaches that of the blood of the fish (about one-third that of sea water). Higher salinities give rise to an increase in toxicity again.

When two poisons occur together they may result in one of three types of mixture having greater (*synergism*), equal (*addition*) or less (*antagonism*) toxicity than would have been predicted from their individual toxicities.

Synergism, fortunately seems rare. It may occur in mixtures of chromium and nickel where some mixtures may be ten or more times as toxic as expected. Antagonism could occur when, for example, an acidic and an alkaline waste come together and neutralise each other.

Luckily for those trying to predict the toxicity of mixtures it is usually the case that additive reactions are the rule, even for chemicals of widely differing toxic action.

There is still a great deal we need to know about the toxicity of poisons to salmonids, to other freshwater fish and to their food organisms. We cannot, by and large, *predict* the toxicity of untried mixtures with assurance; we have to proceed empirically.

5.3   Biological Pollutants

As far as fish are concerned this term could be used to cover both fish pathogens and the introductions of alien species or races where either threaten the genetic integrity of native stocks or could prey on them. As such it has been discussed in 4.2.7 and 4.2.8 and needs no further treatment here.

6.   INDICATORS OF POLLUTION

6.1   Introduction

Given that

(i)   we would find it extremely difficult and expensive to carry out a comprehensive programme of chemical sampling,

(ii)   even if we could the previous section shows how hard it would be to interpret the results in terms of likely impact and

(iii)   pollution is an intermittent process so that our sampling programme would have to be almost continuous,

there is a useful role for a biological system for monitoring the state of pollution of a water. After all, most often we observe pollution as an effect on the biota. The aquatic community responds to, and integrates the natural and polluting factors it experiences.

6.2   Chemical Conditions

To introduce the subject of biotic indices of pollution it is convenient to consider the effects of a gross organic waste on a stream - the damage it causes and the recovery process. Assume that the stream is in excellent condition before the pollutants enter, that they enter continuously and that they are sufficient to cause the most severe state of pollution just downstream of the point of discharge. Figure 5 summarises the chemical conditions which are found and which will now be described.

Upstream of the discharge there will be plenty of oxygen in the water, very little ammonia or nitrite and a little nitrate and organic matter (expressed here as Biochemical Oxygen Demand - BOD).

The effluent enters the stream, probably already loaded with micro-organisms, utilising the organic waste. At first, but not for long in time or distance, aerobic (oxygen-using) bacteria continue to utilise the organic matter. Soon, though, the demand for oxygen, the BOD, has risen so markedly that the DO plunges to zero, except perhaps for a few millimetres near the water surface where reaeration from the atmosphere can still occur.

The waste water contains ammonia but no oxidised nitrogen, and the bacteria use up the oxygen combined as nitrite and nitrate from upstream. Others then utilise the oxygen in the sulphates, reducing them to sulphides. All the oxygen has been used: anaerobic conditions now exist.

The stream remains anaerobic for some distance but the organic waste is being consumed by anaerobic bacteria and so the organic content begins to fall. In this reach carbohydrates are being reduced to *volatile acids* (such as acetic) and these are being further reduced to methane, CH_4. (The bacteria which carry out these conversion are the same species as those in the first three stomachs of a ruminant.) The waste products from the anaerobic bacterial metabolism are nitrogen, methane and hydrogen sulphide. The H_2S gives the stream a foul smell. All three can be seen bubbling to the surface, and methane 'marsh gas' can spontaneously ignite to give the eerie 'Will o' the Wisp', a flickering blue flame.

Fate of carbon, nitrogen and sulphur
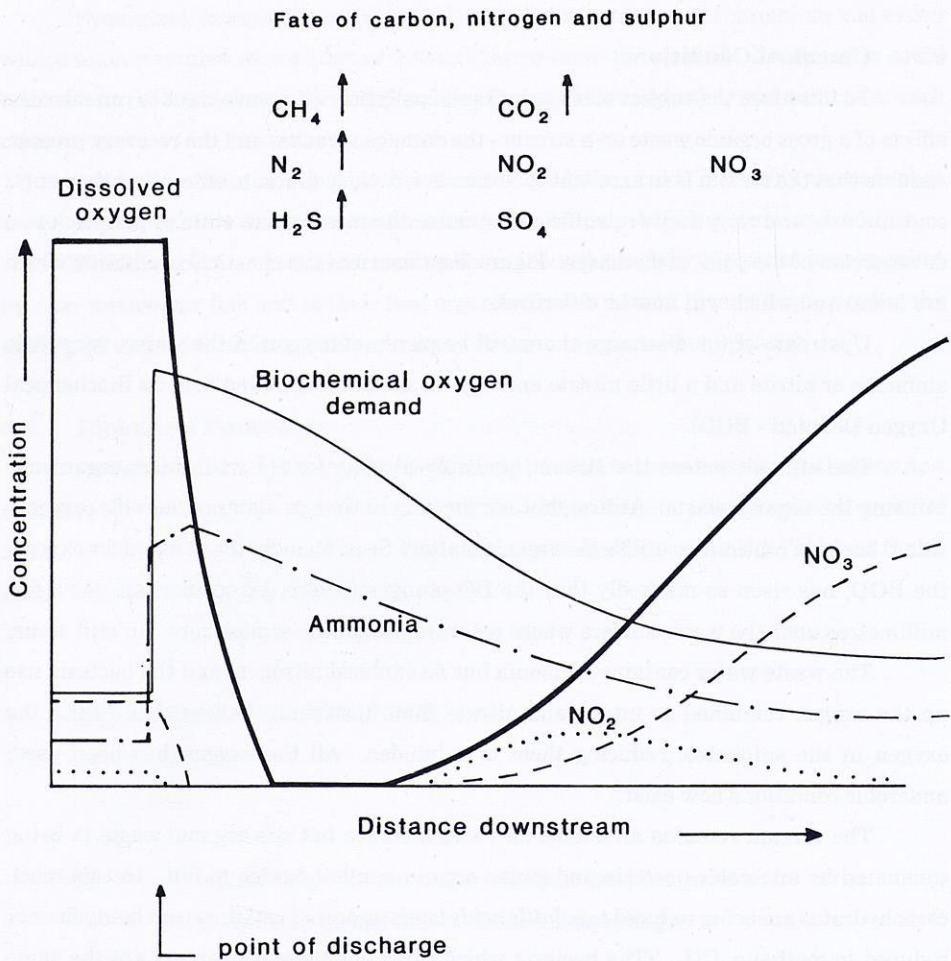
Figure 5. Conditions in the vicinity of a gross organic discharge

With further degradation a little downstream the balance between supply of oxygen and demand is sufficient for oxygen in low concentration to penetrate to greater depth. Now aerobic processes play an increasingly important role and compounds containing carbon, nitrogen and sulphur are oxidised to carbon dioxide, nitrite and sulphate respectively. Ammonia is now declining, oxygen increasing, but nitrate has not yet reappeared; this comes next, and both ammonia and nitrite decrease. The wastes have become *mineralised* so that apart from elevated levels of nitrate and phosphate the stream is restored to its unpolluted state, although in the mud anaerobic processes continue.

The curve described by the concentration of oxygen is known as the *oxygen sag curve*. The length of the sag depends on the strength of the organic waste, its mass, the dilution available and any enhancement of reaeration by turbulence, especially at weirs.

If Figure 5 is turned through 90° clockwise it demonstrates the reactions which occur in a heavily loaded percolating filter in a sewage treatment works. The natural ventilation of the filter is so great that its depth, 2 metres, is generally enough for the purification of the sewage to have reached the nitrate stage before the effluent leaves the bottom of the filter. The speed of reaction is so high that the 'half-life'[Note 38] of the degradable organics in an efficient filter is only 11 minutes!

To summarise the conditions facing any potential colonisers, the stream represents a hostile anaerobic environment with an abundant food supply, leading to a poorly, then better, oxygenated zone where food is still plentiful. This state leads in turn to a reach where phosphate and nitrate concentrations are high but there is little organic waste left to utilise.

6.3   Biological Responses

Under the circumstances described in 6.2 the following sequence of biological events can be found.

In the anaerobic zone there will be vast numbers of anaerobic bacteria, but also, if the stream is very slow moving, or if the polluted water is a pond, a small number of species of air-breathing maggots (fly larvae) may be found. The best adapted of these is the *rat-tailed maggot* of the hover fly *Eristalis*, labelled E in Figure 6. (It grows into an excellent likeness of a honey bee when adult.) The maggot's head is buried in the rich food supply at

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[Note 38] The 'half-life' of an organic chemical is simply the time taken for half its mass to be broken down.

the bottom of the pond or stream but it draws air down through the long snorkel of its *respiratory siphon* to sustain its aerobic metabolism.

Next downstream, where a little oxygen occurs, five typical organisms may be found. These are tubificid worms, Chironomid (midge) larvae, known as *blood worms*, a leech, the water hog louse *Asellus* and 'sewage fungus'. Just as blood worms are not worms but fly larvae, so sewage fungus is not a fungus but a colonial bacterium - *Sphaerotilus*. It looks like a greyish brown growth of cotton wool clinging to objects in the water. It is an important species, producing both good and bad effects. On the credit side it is acting as green plants do - in trapping one form of energy so that it can be handed on to other species in the *food web*[Note 22]. The energy is not, as in the case of green plants, sunlight, but large dissolved molecules of energy-rich organic matter which higher organisms cannot utilise in the dissolved form. *Sphaerotilus* converts these dissolved substances into solid food (and usefully 'wastes' some of the organics converting them into carbon dioxide during metabolism).

An assemblage of species takes advantage of the food supply and shelter which the cotton-woolly bacterial mycelium represents.

The disadvantages of *Sphaerotilus*, apart from the fact that it doesn't look very nice, is that it can slough off and roll away downstream to previously unpolluted reaches where it rots and causes an oxygen demand.

Tubificids and chironomids do not have the advantage of respiratory siphons but they can live in running waters in tunnels or tubes in the surface of the mud. They manage to survive here because they possess a rich supply of haemoglobin with its great ability to take up oxygen even from water containing very low concentrations of DO. These two groups of species can occur in very large numbers - hundreds of thousands per square metre. Already a principle is beginning to appear: the few species which can tolerate gross organic pollution have so abundant a food supply available that very great numbers, or biomass, can occur. Diversity and biomass seem to be inversely related.

Towards the downstream end of the '*Sphaerotilus zone*' algae will begin to appear, utilising the phosphate and nitrate released from the wastes by mineralisation. Again they may succeed in very large numbers - blue-greens first (possibly producing toxins, Note 34) and then green algae. All the problems which accompany eutrophication may now occur, but the plants do have a nett benefit, putting much more oxygen into the system than they

Figure 6. Biological Monitoring Working Party Scores
(for explanation see text)
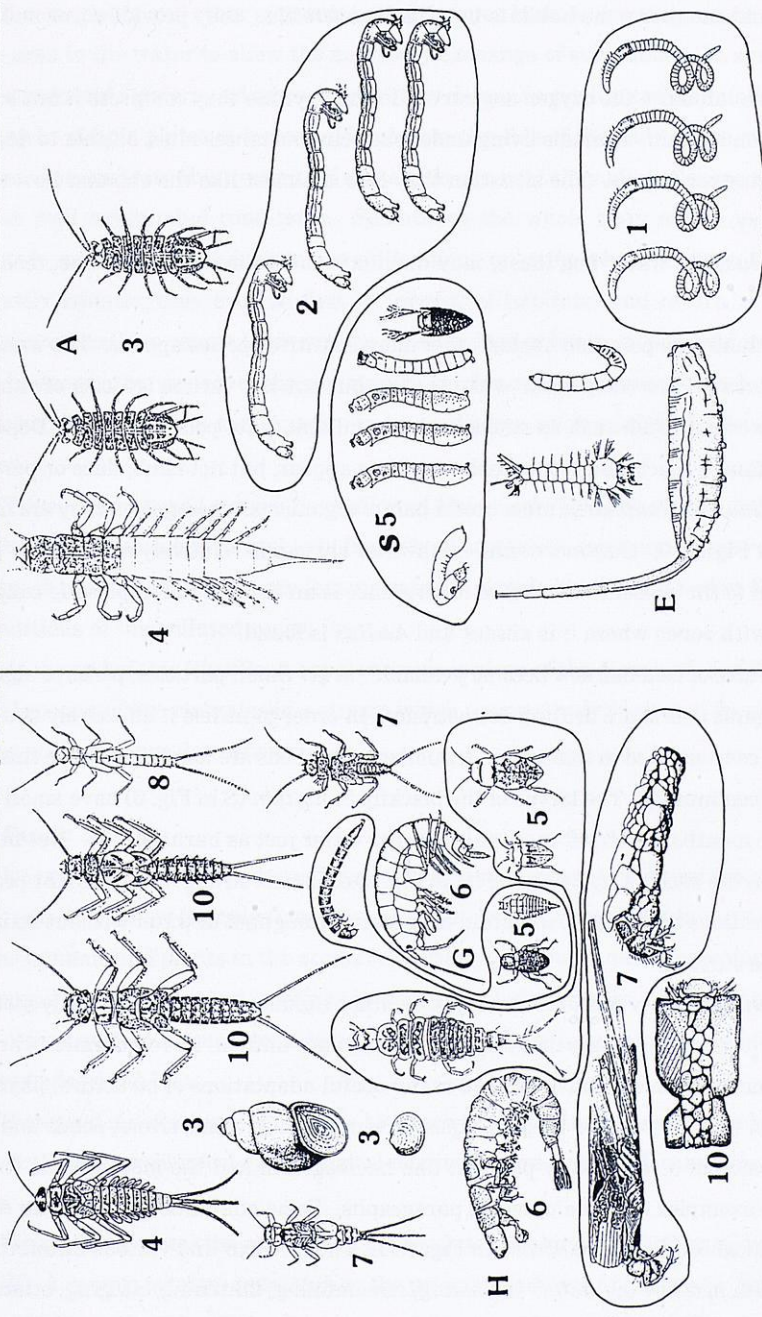
	TOTAL SCORE	91	15
	Av. SCORE PER TAXON	6.5	3.0

remove in respiration. Filamentous algae like blanket weed (*Cladophora*) may look unsightly and smother some habitats but, like *Sphaerotilus*, they provide cover and a food supply.

Algae influence the oxygen sag curve. In the daytime they compress it but at night they lengthen it again. Animals living under such circumstances must be able to deal with such changing conditions. The situation they face is almost like the ebb and flow of tides in an estuary.

Asellus, the water hog louse, may dominate the animals in this zone, feeding on detritus.

Gradually, as pollution abates, other more sensitive species appear. The wandering snail *Limnaea pereger* may occur with *Asellus*, but not the various species of ramshorn snails (*Planorbis*). Fish such as stickleback can inhabit quite polluted zones. Depending on circumstances roach and stone loach may then appear, but not chub, dace or perch yet.

Asellus and *Gammarus* are a useful pair of organisms to recognise: they are marked A and G in Figure 6. *Gammarus* the freshwater shrimp is relatively sensitive to lack of oxygen (and to the presence of zinc) so its presence is an indicator of improving conditions compared with zones where it is absent and *Asellus* is found.

A source of food has now become available - *drift*. Small particles, perhaps algal cells or other organic debris are drifting downstream. In order to utilise it effectively the debris needs to be concentrated in some way. A number of methods are found to achieve this in the freshwater community. The larvae of the blackfly *Simulium* (S in Fig. 6) have small sieves above their mouths which sift material from the water just as barnacles do. Net-building caddis fly larvae such as *Hydropsyche* (H in Fig. 6) construct strong nets of silk at precisely the right locations on stones to maintain maximum throughput of water without being torn away by the current.

As water quality continues to improve, other caddis, mayflies and finally stoneflies appear, each species or family delaying its reappearance until all its requirements are met.

Aquatic organisms have evolved many useful adaptations of structure, physiology or behaviour in order to allow them to exploit or survive in streams, rivers, ponds and lakes. The possession of a respiratory pigment like haemoglobin and the mechanisms for filter feeding are examples from the previous paragraphs. Some adaptations let species exist in all the physical conditions indicated in Figure 1. Thus we can find various different ways of coping with fast-flowing water: ballasting, streamlining, flattening, clinging, attachment to the bed of the river or powerful swimming. In the same way there are several methods

seen for acquiring oxygen and getting rid of gaseous waste products from respiration: as well as haemoglobin and other pigments, gill structures have evolved to present a sufficient surface area to the water to allow the necessary exchange of substances. In species living in well-oxygenated waters and whose respiratory demands are limited by small body sizes gills may be simple plates of tissue held out from the side of the body; some mayflies and stoneflies demonstrate this system. If these gills can beat they allow the species to move into less well oxygenated conditions. Sometimes the whole body moves to create the respiratory current. Some insects are still reliant on atmospheric oxygen (insects are secondarily aquatic; they evolved first in terrestrial habitats) and return to the water surface periodically to renew their surface covering (water boatmen are good examples).

In every other aspect of the community similar adaptations are found, so that the freshwater ecosystem has the capacity to be as diverse as any other, in the absence of pollution.

Time, distance and oxygen have allowed the grossly polluted stream to recover. A full, balanced fish fauna is now able to flourish. The aquatic community has regained its diversity, although it may no longer demonstrate the elevated biomass it had in the organic-rich conditions of the polluted zones.

At the end of this Blue Book a real example is given of the distribution of the fish and principal species of invertebrates in a stream which progressively recovered from industrial pollution with distance downstream.

6.4   Biotic Indices

It is possible to monitor the water quality in a stream using chemical tests, but these have certain limitations (samples may miss an event, or the 'wrong' pollutant may be tested for). The animals and plants in the stream experience the water quality continuously and may respond to it, 'integrating' its effects by gaining or losing species. In fact the life of the stream corresponds to its short-term 'memory', just as the sediments in a lake do over much longer periods (see 2.1.4).

Biological monitoring is the means by which the short-term memory can be recalled. Ideally, both physico/chemical and biological monitoring are employed, complementing one another.

Figure 6 illustrates the commonest approach to biological monitoring of fresh waters in the UK. A sample is taken representing the principal habitats of the reach. The animals are identified, mostly to family level and a score is allocated to each level. These scores are

summed to give the *Biological Monitoring Working Party Score*. The number assigned to a level has been agreed nationally so that a level scoring 10 is most sensitive and one scoring 1 is least sensitive. Some species (eg *Eristalis*) are not used in the score.

The BMWP Score may therefore be any number from 0 to several hundred. In the left-hand half of Figure 6 the sample shown gives a Score of 91. The right-hand sample gives a Score of 15. The higher the number the better the stream would appear to be, but not necessarily so. If a high altitude stream was sampled it is possible that the water was so poor in nutrients that it could only support a few, albeit very sensitive, species. Conversely, another stream polluted to some extent might only be inhabited by tolerant species each scoring 1, 2 or 3, but together making up quite a respectable Score. A refinement overcomes this problem. The total Score is divided by the number of numbers it is made up from. Using the right-hand half of Figure 6 as an example, the Score of 15 is made up of the five numbers 4, 3, 5, 2 and 1; $15 \div 5 = 3.0$. On the left-hand side 91 is made up of 14 numbers; $91 \div 14 = 6.5$. The numbers 3.0 and 6.5 are called the *Average Score Per Taxon* or ASPT. Now it can clearly be seen that the two samples are from communities of quite different sensitivities.

Water industry biologists report the biological state of their monitoring sites in this way across the country, and this helps to maintain national surveillance of our waters, to record their quality and to follow the progress of the industry in attempting to bring all waters to an appropriate state.

7   WATER QUALITY LEGISLATION

Many legal instruments of the European Commission, Council and Parliament relate specifically to water quality. Council Directives bind the Member States to achieve certain results but leave it to the States themselves to choose how to implement the Directives.

The Government may designate Competent Authorities to operate the Directives. In England and Wales (with comparable legislation in Scotland and Northern Ireland) the competent authority is generally the Environment Agency, formed in 1996 by merging the former National Rivers Authority and Her Majesty's Inspectorate of Pollution, which utilises the powers provided by the Rivers (Prevention of Pollution) Acts 1951 to 1961, the Water Act 1973, the Control of Pollution Act 1974 and the Water Resources Act 1991. In Scotland the regional authorities of the Scottish Environmental Protection Agency have taken over the responsibilities of the River Purification Boards.

For fisheries the above Acts and the Salmon and Fresh Water Fisheries Act 1973 are relevant, but also there are aspects of the Wildlife and Countryside Act 1981 and its 1986 Amendment which are important for the protection of fish.

Two pieces of national and international legislation are vital for the freshwater stages of salmonid fish. These are the statement that authorities should *"maintain, improve and develop"* freshwater, salmon and eel fisheries within their areas, and secondly the principal Directive already much quoted in this Blue Book: *'78/659/EEC Council Directive of 18 July 1978 on the quality of fresh waters needing protection or improvement in order to support fish life'*. Most of the limit values have already been mentioned in Section 5 or may be found in Appendix B. The Directive was largely based on the reports of the European Inland Fisheries Advisory Commission available up to 1977. Probably for this reason the Directive does not include limits for the substances which have been the subject of reports published since 1977 - on cadmium, mixtures, chromium, nickel, nitrite and aluminium. Since cadmium is listed in the Dangerous Substances Directive as a List I substance it does not need to be included. The EIFAC report on nitrite appeared in 1984 but a value does appear in the Directive (see 5.2.8).

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APPENDIX A

Pollution by Industry

Since salmon and trout can inhabit a wide range of rivers, the whole spectrum of industrial activity has been summarised, albeit briefly. The structure of this Appendix is simply designed to cover the winning of the raw materials and then their utilisation in manufacture. Inorganic resources - iron, other metals, china clay, building materials - and organics - coal, oil, wood and foods - are discussed.

A.1   Mineral exploitation

The extraction, concentration and other purification of sands, gravels, limestone or granite may all involve water. Coal mines, as an example, require constant drainage, often of a strong chloride water or an acid ferruginous water. Once the coal has been brought to the surface it may be crushed and washed to remove the clay-like impurities.

In china-clay mining, by contrast, it is the clay which is wanted after the quarry face has been eroded by a high-pressure jet of water, the 'monitor'. The problem here is to separate out the micaceous sands in which the valuable clays are found.

Spoil heaps from coal mines, china clay pits and metalliferous mines can all be leached by rainfall. Sulphides in some will be oxidised to give sulphuric acid and thus create conditions for further leaching processes. The metal leaching from the heap may be unexploitable, occurring in currently uneconomic quantities; zinc from the lead mines of mid-Wales would be an example.

Alternatively the cause of pollution from metalliferous mines, as from stone quarries, might be inert suspended solids.

Oil wells on land, without proper provision for minimising damage to the environment, could be a good example of problems brought about by a changing land use rather than the new use once established. The preparation of the site and drilling the well are likely to be far more disruptive than the extra road usage by a few tankers a week to collect the oil.

In the case of coal mines, and perhaps certain metalliferous mines, a particular set of problems occurs after the mine has been worked out. Water continues to enter the abandoned workings but is no longer pumped out and gradually fills the mine. If it becomes acidic, as it often does, it dissolves iron and other metals. Eventually the drainage water 'breaks out' at the surface and can destroy a river overnight. The iron may precipitate out on exposure of the mine drainage to the air, and blanket the receiving water in ochre. The

precipitate, the acidity and the dissolved metals all contribute to exceptionally toxic conditions.

A.2   **Heavy production industry**

As with mineral exploitation, water becomes contaminated in many ways by the traditional 'heavy' production industries. For example, a fully integrated steel works would need water to quench the coke from coke ovens when making blast-furnace gas, to cool the outer casing of the blast furnace in order to prolong the life of its refractory lining, to clean the flue gases before their re-use, to cool the oxygen-injecting lances in the steel-making plant and the rollers in the strip-rolling mills and finally to cause the hot strips to roll up into giant 'watch springs'. In such uses the water would become contaminated with ammonia, phenols, metals, oils and heat.

Metal plating and processing may cause cyanides, acids and organic solvents to enter the waste waters from the factory. Solvents such as chlorinated compounds are a particular concern in the ground water below many conurbations.

A.3   **Chemical industry**

Primary producers of chemicals convert raw materials like oil into the starting-point compounds of many secondary products, which can then be utilised by the manufacturers of plastic articles and synthetic fabrics, pharmaceuticals and household products. As the chain of events lengthens between raw material and finished product the multiplication of chemical types proceeds at an increasing rate. Inevitably, waste products and useful but accidentally spilled chemicals may reach watercourses. Figure 3 indicates some of the routes of chemicals to a receiving water.

A.4   **Textiles**

Both natural and artificial materials may need to be dyed, and the former to be proofed against the attacks of pests. Dyes and pesticides may appear in the waste water discharges of the industry, often intermittently because they are used in batches. It may be particularly difficult to control such pollution where the fleeces or cotton have been treated abroad (as with dieldrin in some fleeces) in countries without adequate limitations on the use of such substances.

A.5 Food

Despite the wholesomeness of the final product, the preparation of foodstuffs for processing may involve pollution. The problem is often one of scale: food processed in the home leads to many small sources of organic contaminants; these are diluted when washed down the sink *en route* to the sewer. Mass releases of vegetable washings, abattoir waste, whey (a by-product from milk processing factories), or the effluents from sugar beet factories or distilleries can pose a far greater burden on the sewage works and the receiving water. Where production runs are seasonal or intermittent the problems increase.

A.6 Pulp, paper and timber products

Finally, to return to the valuable but potentially polluting forest products industry, in converting the raw material into newsprint, cardboard or building materials, suspended solids (often fibrous), organics, alkalis and pesticide residues may be discharged to the sewer or surface waters.

APPENDIX B

The Toxicity of Metals to Fish

In the short introduction to the Section on Metals (5.2.6) the reader was left with a note that generally metals are more toxic in soft water than in harder water.

This is not just due to precipitation of the metal as carbonates etc, but is still the case when the remaining metal in solution is considered. It seems (perhaps among other reasons) that calcium and magnesium protect certain sites on vulnerable enzymes. These sites include the active sulphydryl (-SH) groups. In high concentrations metals may cause such severe local damage (eg asphyxiation from excessive production of mucus) that the systemic damage never becomes apparent. For many substances the mechanisms of acute (short-term) and chronic (long-term) toxicity may be quite different. Notes on particular metals now follow.

B.1   Aluminium, Al

Aluminium is involved or suspected of involvement in a number of human ailments - Alzheimer's Disease, senile dementia, Parkinson's Disease. In fresh waters it may affect the environment when released from soils by acid rain (4.2.5) or when accidentally discharged from waterworks using alum as a flocculent to remove suspended solids from potable supply. In the latter case the damage is more likely to be caused by the physical properties of the alum sludge - coating and causing malfunction of delicate membranes. In acidic waters acute and chronic symptoms may be seen. EIFAC (Howells *et al.*, 1994) found it most useful to refer to proposed standards in terms of the soluble inorganic forms of aluminium, with one exception mentioned later[Note 39]. In very soft and acidic waters where there was less than 2 part per million (mg/l) of calcium in the water, the proposal was that the maximum safe levels of aluminium lay between 15 and 75 parts per billion (µg/l), depending on pH. If there was more than 5 mg/l of calcium present the values of aluminium ranged from 30 to 100 µg/l, again depending on pH but also on the amount of silicon present. Above pH 6.5 standards should be set in terms of total aluminium and 1 mg/l was considered safe.

[Note 39]   When describing the forms a metal may take in solution we distinguish *species* from *fractions*. For example, fractions are defined by the operation needed to distinguish them - such as 'total soluble metal', 'monomers', 'polymers'. Species are the precise atomic or ionic configurations - Al^{+++}, Cu^{++}, $ZnCO_3$. In fact we have no agreed methods for determining the species of aluminium in water. Instead, the species are calculated using thermodynamic principles and stability constants for a hoped-for equilibrium.

B.2   Cadmium, Cd

Even in hard waters the long-term toxic concentrations of cadmium are very low. EIFAC recommended (very tentatively) that for rainbow trout (and thus salmon), the 95 percentile in water of hardness 100 mg/l as calcium carbonate ($CaCO_3$) (a medium hardness) should be no more than 1 µg/l. To kill fish in short-term exposure much higher concentrations of cadmium are needed.

We are still uncertain of how cadmium kills fish, but we do know one of the defence mechanisms, at least for rainbow trout, roach and stone loach. The mechanism depends on proteins whose normal role is the storage of useful metals[Note 40].

Cadmium is a List I metal - see Mercury, below.

B.3   Chromium, Cr

Chromium is one of those metals which exert their toxic action in the anodic form (Cr_2O_7). Arsenic is another example. Chromium can exist in the trivalent form (Cr^{+++}), but, like chlorine, this is a transient species except in waters of low pH. Chromium occurs in effluents containing plating or tannery wastes.

EIFAC's recommendation on chromium is that waters for salmonids should not contain more than 25 µg/l as a mean, and the 95 percentile should not exceed 100 µg/l.

B.4   Copper, Cu

The cupric ion, Cu^{++}, is the species toxic to fish. Copper may easily become bound to organic materials like humic acids or adsorbed onto suspended solids. Therefore, when setting standards for copper it is only the cupric ion which must be considered and not the broader fractions such as 'total dissolved copper' etc.

The EC Directive recognised the importance of hardness in setting out four different guideline values for salmonid waters, ranging from 5 µg/l for very soft waters (10 mg/l as

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[Note 40]   If trout are placed in clean water without zinc but with added cadmium they die at concentrations as low as 15 µg/l and are unable to breed at 2 µg/l. The cadmium entering the fish is bound by two acidic proteins and accumulates to a lethal extent in the kidney, liver and gill. (Roach and stone loach under these circumstances can survive up to 650 and 2000 µg/l respectively. In their case the cadmium induces the synthesis of a protein different from the two trout proteins, which can be excreted - so it never reaches toxic levels except in the most extreme of circumstances.)

Under normal conditions cadmium occurs with traces of zinc. If we simulate this condition in the laboratory we find that the trout survive 15 and even 34 µg/l of cadmium. The reason that they now survive is that zinc switches on the synthesis of two forms of a protein that bind cadmium and *can* be excreted.

CaCO₃) to 112 µg/l for hard waters (300 mg/l as CaCO₃). The Directive also appreciated that where fish were present in waters containing more copper than the appropriate guideline value the cause of the discrepancy might be organic complexation of the copper.

B.5   Iron, Fe

As indicated above, iron can only exist in solution at toxic concentrations in waters that are already dangerously acidic for fish. Such conditions are normally transient because the iron-rich water, on reaching the surface where oxidation can occur, precipitates out the iron as ferric oxide, red ochre.

B.6   Lead, Pb

Fish affected by lead poisoning may show considerable discolouration or spinal deformities. In the UK the effects of lead in streams have been studied the longest in Wales, where observations on the Rheidol system began in 1922. The lead leached from spoil heaps containing galena (lead sulphide). These gradually become oxidised and leached out, reducing the concentrations of dissolved lead over the years. As the lead (and the accompanying zinc) decreased so plants and animals recolonised the river.

For rainbow trout in water of medium softness (50 mg/l as $CaCO_3$) toxic levels will be around 1 mg/l in exposure periods lasting 48 hours.

B.7   Mercury, Hg

Mercury is exceptionally toxic, but not as the elemental form if taken by mouth. The 'mad hatters' bear witness to the toxicity of the vapour however. In the infamous Minamata Disease of 1953 the symptoms were largely neurological too but teratogenic[Note 41] responses were also seen. The source was a plastics factory which had discharged 600 tonnes of mercury into Minamata Bay, but in an inorganic form, unknown for clinical effects of such severity.

The answer to the puzzle came in 1969 from Swedish studies on the increased death rate of fish-eating birds. Thanks to the analytical method *gas chromatography* the mercury was found not to be inorganic but the organic compound dimethylmercury. It was not discharged as this compound but as inorganic mercurial salts from wood pulp factories

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[Note 41] *Teratogenic*; giving rise to monsters, ie deformities in the foetus (Gr. *teras*, a monster).

(4.2.3). Anaerobic bacteria in the muds of the lakes receiving the wastes were responsible for the conversion.

Thus the *bioaccumulation* of mercury (and all other materials) depends on its *bioavailability*. Dimethylmercury was more available than inorganic mercury. The reason for this is that the organic form was *readily soluble in fats*. This important characteristic has been referred to in the brief account of organic pesticides (5.2.14, above).

Mercury and cadmium are known as 'List I' metals in the EEC, and as such, Member States have committed themselves to eliminate pollution caused by such Dangerous Substances.

B.8   Nickel, Ni

The chemistry of nickel in fresh waters is considered to be fairly simple, in that all the soluble inorganic species have a similar toxicity.

The metal demonstrates local and systemic poisoning, like cadmium, but not necessarily through the same mechanisms.

EIFAC tentative standards do not distinguish between salmonid and non-salmonid waters but separate standards *are* recommended for hard and soft waters. The average concentration of soluble nickel should not exceed 10 µg/l and the 95 percentile should not exceed 30 µg/l in soft water (20 mg/l as $CaCO_3$). In hard water (320 mg/l as $CaCO_3$) the corresponding concentrations should be 40 and 120 µg/l respectively. Where complexation with organic material may occur, higher concentrations may still be satisfactory for fish and their food.

B.9   Zinc, Zn

Zinc must be among the most studied of heavy metals in relation to toxicity to fish. The EC Directive sets mandatory values from 30 to 500 µg/l for salmonid waters with hardness values from 10 to 500 mg/l as $CaCO_3$. Unlike copper, it is not just the divalent ion (Zn^{++}) which seems to be toxic. Finely divided zinc carbonate seems toxic too, even though, at least outside the gill chamber, it is not in true solution.

Zinc is accumulated by fish to levels that reflect the ambient concentration[Note 42].

[Note 42] Roach in the Willow Brook, Northants, contained much lower concentrations of zinc in all tissues (except the eye) after a major pollution problem was solved and ambient concentrations fell from 3.3 to 0.2 mg Zn/l. (The eye contains carbonic anhydrase which is rich in zinc.)

Some invertebrates are very tolerant of most inorganic pollutants but the freshwater shrimp *Gammarus* is more sensitive to zinc than trout is. So is stone loach, despite being far more resistant to cadmium. Such details of the different sensitivities of species are used for invertebrates in formulating *biotic indices*.

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Sequence of fish species and principal invertebrates (not to scale) as pollution lessens with distance downstream. Horizontal lines show location of species. Sloping line represents degree of contamination of water.
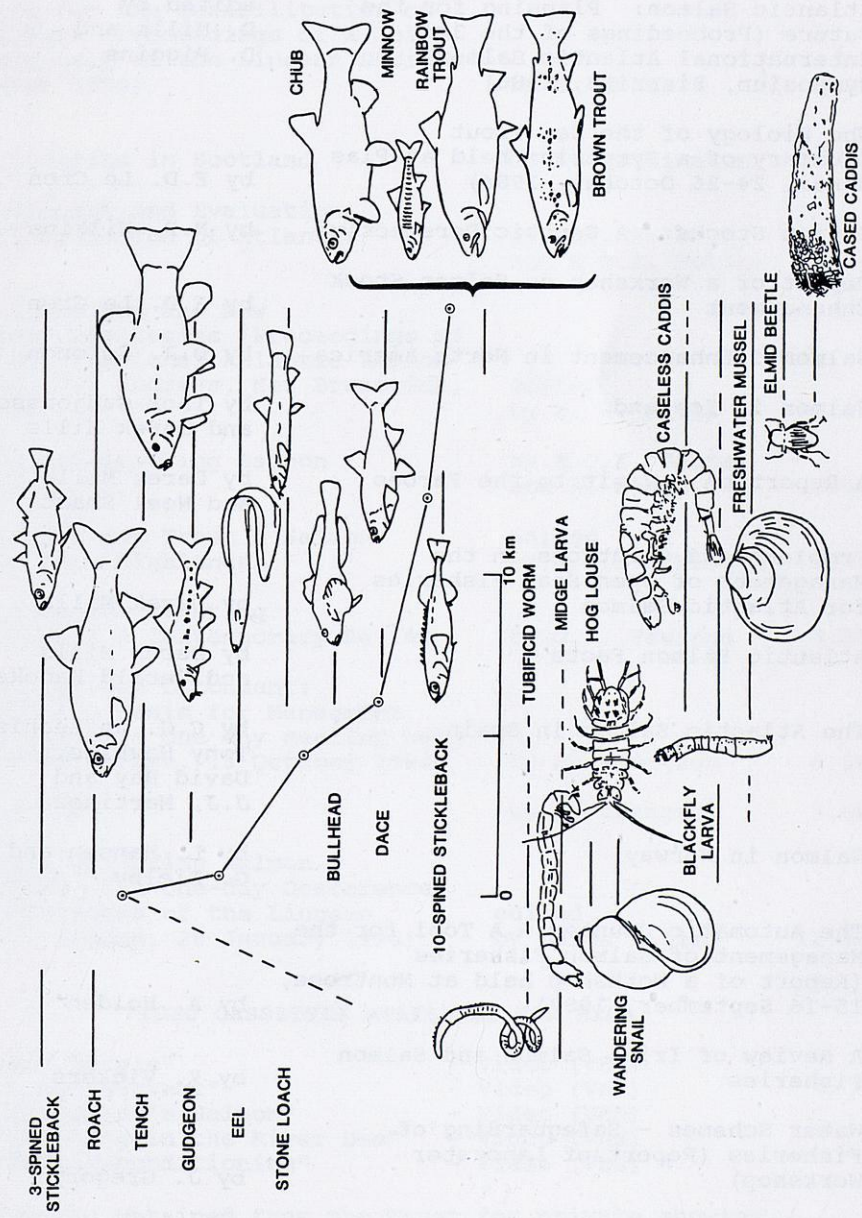
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