ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

Stream quality in a small urbanised catchment

Matthew Thomas Robson

A thesis submitted in partial fulfilment of the requirements of Sheffield Hallam University for the degree of Doctor of Philosophy

September 2004

Abstract

River-length patterns in the chemistry and biology of the Charlton Brook, an unclassified watercourse in northwest Sheffield have been examined. Sampling sites for macroinvertebrates and pollutant analysis were used, in conjunction with Environment Agency General Quality Assessment (GQA) methodologies and hydraulic analysis of the catchment. Sites were strategically located to account for the tributaries and the brook downstream of their confluence, to assess the potential impact from surface water outfalls (SWOs).

Variations in GQA parameters indicate a significant drop in quality downstream of the SWOs that discharge to the study watercourse, with a marked drop in biological diversity noted at the onset of urbanisation. The decline in biological quality however, is greater than that suggested by physico-chemical analysis alone. There was a significant inverse relationship between impermeable area and biological diversity.

Analysis of polycyclic aromatic hydrocarbons (PAHs) and trace metals in sediment from the watercourse showed significant, yet irregular between site variations. PAHs in conjunction with metals as a function of the PEL-quotient method employed, suggest that all the sites sampled for macroinvertebrates have the potential for being adversely affected by the pollutants contained within the brook's sediment. Mean PEL-quotients suggest that sediment contamination within the brook is indicated at all sites.

The potential toxicity of instream metal concentrations was determined using cumulative criterion unit (CCU) scores. CCU analysis highlighted cadmium, copper and lead as the major sources of potential instream toxicity with all sites exceeding the threshold for likely harm to aquatic life.

In the absence of different physical characteristics, comparisons of the chemical and biological data indicate that the benthic macroinvertebrate population of such watercourses are adversely affected by the stormwater inputs.

Acknowledgements

This study, which took place within the Charlton Brook catchment in Sheffield, was carried out under a research studentship funded by the School of Environment and Development, Sheffield Hallam University. This undertaking would not have been possible without the help of a number of people and it is fitting that their efforts are recognised.

I am particularly indebted to Dr. Kevin Spence for his patient support, enthusiasm and constructive advice, without whom; this work would not have been possible. Special thanks are also due to Paul Flanagan, for the manufacture of apparatus, and assistance with equipment installation. I would also like to thank Dr. Ian Guymer, Dr Peter Drew, Dr. Phillip Gardner, Mr. Jason Drake, Mr Nelson Chilengwe and all the technical support staff for the loan of additional equipment and the use of their facilities.

Lindsey Beech assisted in the early identification of macroinvertebrates and subsequent quality control of samples, Gemma Bird assisted with site surveys and Thomas Robson braved inclement weather to assist with the collection of stormwater samples. Thanks are also due to Mr & Mrs Geoff Ali, Mrs Margaret Ridge, Rainbow Kennels, Lound Infant School and Yorkshire Water for allowing the siting of equipment on their property. I would also like to thank my family and friends for their support, particularly my mother Stella, and Thomas, Louis and Francesca for putting up with their father's obsession.

Except where specific reference has been made to the work of others, this thesis is the result of my own work. It has not, either in part or whole, been submitted to another academic institution for a degree or any other qualification.

Contents

Figures

Tables

Plates

Chapter 1

Introduction

1.1 Introduction

Although there has been much attention on the decline in water quality and its ecological consequences in larger rivers...small urban streams are essential, albeit often unrecognised, elements of urban rivers (Meyer *et al.*, 2003). Indeed, many such small streams, far from being treasured links in a mosaic of interdependent habitats, appear to be valued for their utility in expediting the removing of questionably contaminated urban runoff.

Small urbanised streams are subject to myriad impacts, including culverting, channel straightening, removal and degradation of riparian vegetation, contaminated discharges, invasion of non-indigenous biota and the construction of paved and hard surfaces that reduce baseflows and increase the likelihood of flooding. The degree of impact associated with these watercourses is poorly understood, yet anticipated increases in urbanisation will likely result in increasingly severe impacts on this largely ignored resource. Comprehensive incorporation of small streams into the legislative framework such as the Water Framework Directive remains to be seen, although there are encouraging signs north of the border, with the Scottish Environmental Protection Agency committed to assessing, at least minimally, all of its unclassified streams and headwaters in the near future.

The impact to small urbanised streams is under-researched in the UK, particularly in the case of urban areas with separate systems of drainage. Therefore, this thesis aims to improve the understanding of such environments.

1.2 Aims and scope of research

This three-year study commenced on the 4 th September 2001. The initial aim was to determine the impact of stormwater discharges to an unclassified river. Implicit in this aim were the following objectives:

- to spatially determine the GQA chemical classification of the brook using Environment Agency protocols.

- Investigate the potential cause of any impairment through determination of the biochemical characteristics of the watercourse.

It was envisaged that the study results would determine whether the arbitrary classification of the brook was an accurate representation of its quality. Minor tributaries are presently assigned the same grade as that given to the stretch of water they feed, under the Environment Agency's GQA scheme. On this basis, Charlton Brook in its entirety is designated a grade C. However, there is general consensus that in attempting to assess the impact of stormwater or other discharges to receiving waters, chemical parameters alone are not sufficient (Johnson *et al.*, 1998; Ellis, 1989; Payne, 1989; Field & Pitt, 1990; Ellis, 1991; Faulkner *et al.*, 2000). Stormwater discharges to watercourses can have physical, chemical and biological impacts, but their intermittent and unpredictable nature makes impacts difficult to assess (Payne & Hedges, 1990). If measured alone, chemical determinants do not give adequate representation of the effects of continuing pollution or the effects of a single incident over time (Beech, 2001). Biological monitoring is valuable in such cases, as stream fauna [and flora], respond to all the stresses placed on them by intermittent discharges and as such provide a measure of the quality or health of riverine ecosystems. Of the wide range of organisms suitable for biological monitoring, benthic macroinvertebrates (> 0.5 mm; Cummins, 1975) are the most widely used because they are found in virtually all waters, are differentially sensitive to various pollutants that occur infrequently or in very low concentrations and respond to stresses quickly. Additionally, macroinvertebrates are reasonably sedentary, with comparatively long lives, so they can be used to assess water quality at a single site over a long period of time (Mason, 1996). Their heterogeneity means that single samples are likely to catch a large number of species from a range of phyla, and it is likely therefore, that at least some species or groups will respond to a particular environmental change (Mason, ibid.).

It is acknowledged that wet-weather discharges (typically in relation to CSOs) can have a disproportionate impact upon river aquatic life (FWR, 1998). However, Bastian (1986) iterates that whilst their amount, form, timing and duration can all be important, it generally makes little difference from a water quality perspective if the sources of excessive pollution come from traditional point sources, urban stormwater

runoff, atmospheric sources, agricultural runoff or other non-point sources. Work by Seager & Abrahams (1990), and latterly by Milne *et al.,* (1992) indicated that storm sewage discharges exert a chronic effect on the benthos up to 250 metres downstream. However, it is less clear whether a higher frequency of events at lower pollutant concentration will result in a similar net impact on aquatic life. Early results suggested that factors other than pollutants determined by the general quality assessment procedure were impacting on the watercourse. Consequently, the aims of the study evolved to additionally include the following objectives;

- determination of the biological quality of the study watercourse.

- to determine the potential toxicity of the benthos in relation to water and sediment quality standards.

During the course of the study, a substantial number of site visits were made to collect water samples for biochemical and inorganic pollutant analysis, sediment samples for metallic and organic micropollutants and biological samples for macroinvertebrate analysis. Similarly, site visits were made in order to sample storm flows within the stream.

During the study, water samples for biochemical quality were collected at four different sites, to reflect the longitudinal course of the stream from its rural headwaters to its urban outfall. Biological samples were taken from seven locations within the catchment. To effect a direct comparison, water and sediment samples collected for inorganic and organic micropollutants were taken from the same locations as the biological samples.

Surveys were made of the site in conjunction with asset data to produce a hydraulic model of the catchment. Empirically derived flow and rainfall data were applied to the model to determine the behaviour of the catchment in relation to stormwater inputs.

The results of the study have been used to describe the potential causes of stream quality impairment within a small urbanised catchment.

Chapter 2

Literature review

2.1 Historical practice

Urban drainage has existed at least since the time of the Mesopotamian Empire some 5,000 years ago, a practice continued by the Minoans, Greeks and Romans. In Rome, parts of the Cloaca Maxima (biggest sewer) started in the 6th century BC and restored by Agrippa *circa.* 33 BC are still in use today. However, the decline of the Roman Empire heralded the decline of sanitation practices with, for example, surface drains conveying surface water to receiving watercourses and bodily waste being deposited into cesspits as was the case in 19th century London. It was only in 1817 that the overflow from cesspits was allowed to be connected to the sewer system in London and not until 1847 that houses were required to be connected directly to the sewers. The consequences of this are well documented. By the 1850's the Thames had become nothing more than a very large open sewer, prompting the sanitation reforms that resulted in Bazalgette's 'combined' interceptor sewers. However, this feat of engineering, the majority of which is still in use today, had simply shifted the problem downwards to the Thames estuary and it was not until the 1970's that fish such as salmon could be found in the river.

Despite the best efforts of Edwin Chadwick (1800 - 1890), the Victorian sanitary reformer who argued for a dual system of drainage; one pipe for rain and one for excreta, the standard practice up until 1945 was to construct combined sewers. These systems by necessity include combined sewer overflows (CSOs) to allow excess water during storms to discharge into receiving watercourses. Although since 1945, the norm has been to drain new developments with a separate system of sewers, the majority of systems (70% by length) in existence in the UK today are combined (Ellis 1989a). The adoption of separately sewered systems was intended to improve on combined systems noted for polluting receiving waters via overflows during storm events. The use of separate sewer systems is intended to reduce the need for those discharges, potentially reducing the pollution discharged to watercourses.

Whatever the arguments for the pros and cons of both systems, there is little likelihood that either system will be completely disregarded in favour of one or the other, rather, future emphasis will more probably be focused on sustainable urban drainage systems (SUDS). One of the major reasons that doubts have arisen with regard to the merits of the separate system is that there is now widespread

acknowledgement that stormwater is not as pure as rain! A "notion that.....should be abandoned from the outset" (Novotny & Chesters 1981).

2.2 The problem of urban stormwater discharges to receiving waters

This practice of discharging urban stormwater directly to receiving waters is acknowledged and referred to extensively throughout the literature, (New South Wales Environmental Protection Agency, 2001; Butler & Davies, 2000; Novotny & Olem, 1994; Field & Turkeltaub, 1980) as has the recognition that urban stormwater runoff is a major cause of impairment to receiving waters, (SEPA 1997; Environment Agency, 1998; United States Environmental Protection Agency, 1990; Myers *et al.*1985). However, it is only since the 1950's and early 1960's that it has been recognised that waters discharged via surface water drains contain contaminants. As Novotny (1995) has stated, it was realised [only in about 1970], that more than half of all pollution originates from sources that are diffuse and difficult to control. The main delivery of non-point pollution to surface water bodies is via urban stormwater runoff and according to D'Arcy (personal communication) it is still regarded as standard practice to discharge urban stormwater directly into receiving waters. In the UK, 30% of total sewerage is fed by separate systems, distinct from combined systems, which comprise a mixture of wastewater and stormwater. Various authors cited by Harrop (1984), all concluded that separate sewerage was unwarranted due to the poor quality of urban runoff.

There is general consensus that stormwater discharges from urbanised catchments to receiving waters are a significant pollutant source (Chocat *et al.*, 2001; van der Heijden *et al.*, 1986; Heaney *et al.*, 1984; U. S. EPA, 1984; Randall & Grizzard, 1983; Field & Turkeltaub, 1980; Sartor & Boyd, 1972) and that the contaminants transported in these discharges are a major source of impairment to the receiving waters (Myers *et al.*, 1985; USEPA, 1990; Makepeace, *et al.*, 1995; Environment Agency, 1998). The 1988 Report to Congress (U.S. EPA, 1990, cited in Novotny & Olem, 1994) stated that urban stormwater runoff was the fourth most extensive cause of the impairment of the United States' rivers, whereas combined sewer overflows were deemed the tenth most significant. Closer to home, it was found that 20% of poor quality waters in Scotland resulted from urban runoff (SEPA, 1996). According to Harrop (1984), stormwater runoff can contribute concentrations greater

than 100 times the levels that are detrimental to the health of freshwater fish. In the UK, despite research to the contrary, it was, according to D'Arcy *et al.* (1998), not until the Forth River Purification Board Initiative that diffuse pollution and BMP structures were considered by the regulators as a serious issue.

Others have been less convinced (Tebbutt, 1998; Lee & Jones-Lee, 1993; Lee & Jones-Lee, 1995). Lee & Jones-Lee (1993), have stated that many of the contaminants associated with urban stormwater runoff do not impair beneficial uses of receiving waters, arguing for example that CSOs deserve special attention, being able to cause 'real water quality problems'. They also concluded that stormwater discharges could possibly exceed water quality criteria without causing adverse impacts due to their episodic nature. The basis for their scepticism was that the criteria were developed by bioassays using bioavailable forms of contaminants and assuming worst or near worst-case exposure conditions and that hence, standards were overly protective to aquatic organisms when applied to total, rather than biologically available concentrations (Novotny & Witte, 1997). Clearly, interpretation of the acute toxicity criteria stated as the 1-hour average concentration not being exceeded more than once every three years on the average, does appear to be overly stringent, as the permissible exceedance equates to only 0.004 % (1 hour in 3 years; Novotny & Witte, ibid). However these conclusions appeared to ignore the chronic impact from sediment-bound pollutants introduced by stormwater such as bioaccumulation and delayed acute response, the potential interaction between individual compounds and the dilution available within the receiving water. Lee & Jones-Lee (1995) also suggest that biological problems in urban receiving waters are mostly associated with illegal discharges and that sediment-bound pollutants pose little risk. However, as Burton *et al.* (2000) have elucidated, this opinion is not supported by field studies, arguing that a growing preponderance of data is showing that toxicity is commonly observed during storm events and that short-term pulse exposures can be more toxic than long-term continuous exposures.

Although receiving waters can assimilate short duration pollutant inputs without damage to their biointegrity given sufficient assimilative capacity (Osborne & Herricks, 1980), even a small load may produce an unacceptable concentration in a small stream where the capacity for dilution is limited (House *et al.*, 1993) and this may be exacerbated further during periods of low flow. Although stormwater is acknowledged as having an adverse impact on receiving waters, it is not considered as

having enough importance (financially or otherwise) to discard the standard practice of discharging to amongst other things, urbanised streams. Yet, discharges to such watercourses are so diffuse and the outfalls so numerous that they cannot according to SEPA (1997), be controlled using numeric consents based on the dilution available in a receiving watercourse. When this approach was extended to surface water outfalls, sufficient dilution was only feasible in the largest of rivers (Hall & Ellis, 1985). Whilst the waste assimilative capacity of surface waters for some contaminants such as biodegradable organic matter may be large, it is much lower or even non-existent for some toxic and carcinogenic cumulative organic chemicals and toxic metals (Novotny & Chesters 1981). Ellis (1991) has suggested that dilution ratios varying between 6: 1 and 600: 1 would be required to reduce the metal concentrations associated with urban discharges, to levels that would conform to allowable annual average or maximum allowable concentrations for freshwater life.

Work by Pascoe & Shazili, (1986) using rainbow trout, *Salmo gairdneri*, showed that irreversible toxic effects initiated during an episodic pollution incident could lead to the death of fish some considerable time after the incident even if normal water quality conditions were restored. For example, a brief episode of 32 minutes exposure to 1.0 mg cadmium l^{-1} was sufficient to bring about the eventual death of 50% of the fish, 175 hours after transfer to clean water, without, it should be noted, the effect of synergism. Similar investigations with Asellus aquaticus (Williams *et al.* 1985) produced analogous results with mortalities still occurring more than 40 days after the laboratory simulated episodic incident with cadmium, making it evident that the toxicity of episodic pollution may be much greater than indicated by conventional toxicity (Pascoe, 1987). Although juveniles are generally more sensitive than adults ,sensitivity also varies with physiological status such as post-moulting or brood carrying adults, leading to the observation that ecological disturbance can result from episodic pollution occurring at a time when such sensitive stages in a species life cycle are abundant (Pascoe, ibid.). Clearly, frequent discharges of any given pollutant concentration, typical of natural systems (i.e. subject to rainfall) may impact on every life cycle stage.

Cumulative loading is also likely to be important as is the frequency of stormwater pulses to the system. Instream responses to such intermittent discharges result from what Ellis & Hvitved-Jacobsen (1996) refer to as process interactions such as transport, dilution, transformation of organic matter, adsorption of metals and die-

off of bacteria. Ellis & Hvitved-Jacobsen (ibid) suggest that although not as severe as CSO discharges, receiving water recovery time for surface water runoff discharges is in the order of 1 to 2 days. So, by way of example, a watercourse experiencing 60 storms in a year could spend up to 4 months of the year recovering. A common view, held by the likes of Tebbutt (1998) that surface waters are relatively clean and can be safely discharged into local watercourses would also appear to be flawed. Despite it being common practice to discharge runoff from combined catchments into the nearest stream, as little as a 2-5% of wrong connections will entirely eliminate the water quality benefits of such separation (Ellis, 1989a). This strain on the theoretical advantages of separate systems is certainly not unique to the UK and has been reported elsewhere (Desbordes & Hemain, 1990). Indeed, illicit discharge connections, leaking sewer systems and failing septic systems are a large and persistent contributor of pollutants to urban streams (Faulkner *et al.*, 2000). Irrespective of un-designated discharges however, there is now overwhelming evidence confirming that runoff alone is sufficient to impact on the quality of rivers.

The mean annual concentration of pollutants from stormwater discharges has been compared to sewage following secondary treatment (Hvitved-Jacobsen, 1986). Yet during storm events, peak concentrations can be much higher than treatment plant discharges. As early as 1972, Sartor & Boyd (1972) calculated (based on a hypothetical yet typical city) that the runoff from the first hour of a 'moderate-to-heavy' storm would contribute considerably more pollutional load than would the same city's sanitary sewage during the same period of time. Saget *et al.* (1998) calculated that the maximum load that could be generated by a rainfall event could reach four and seven times that from a treatment plant for BOD and COD respectively and that for suspended solids, the maximum load generated by a rain event may be as much as 26 times the dry weather load from a treatment plant. These impacts would, it is argued, be even worse if applied to other pollutants such as heavy metals and hydrocarbons due to their greater concentration in runoff than industrial and domestic sewage (Saget *et al.*, ibid.). As Ellis & Hvitved-Jacobsen (1996) have argued, although pollutant concentrations are generally lower compared to CSOs, due to the relatively higher amount of water volume discharged on an annual basis, both heavy metals and organic micropollutants may be important. Carleton (1990) carried out a comparative study of combined and separate sewer systems in France and Australia. He concluded that the use of separate sewerage systems to solve pollution

problems might not be justified, according with the aforementioned conclusions that annual pollutant loads from separate system overflows were higher than that for combined systems. However, the state of affairs within these two broad schools of thought is complex, not least because the consideration of stormwater discharges as a polluting source, or otherwise; in isolation, is rare in the literature.

2.3 Contaminants found in urban stormwater

The contaminants contained within stormwater have been extensively studied with reports identifying the melange of pollutants present (Ellis, 1989b; Muschack, 1990) and typically, they can be classified under the following headings; after Randall and Grizzard, (1983).

- Suspended sediment;
- Oxygen-demanding substances;
- Heavy metals;
- Toxic organics - pesticides, PCBs;
- Nutrients - nitrogen, phosphorous;
- Bacteria and viruses;
- Petroleum - based substances or hydrocarbons;
- Acids;
- Humic substances;
- Thermal enrichment.

Suspended sediment

Suspended sediment is the ubiquitous contaminant in urban stormwater and has consequently received much attention in the research. Sediment loadings of stormwater are regularly found to exceed those in CSO and other point sources of discharge (Field & Turkeltaub, 1981; Wilkinson, 1955) and are highly variable in concentration (Bastian, 1986; Andoh, 1994), and composition. The earliest studies into urban stormwater highlighted this fact; Wilkinson (1955) noted suspended solid loads of up to 2045 mg/l from a 247 ha. housing estate. However, Ellis (1979) in his study of the Graham Park Catchment, recorded concentrations of between 85 to 4500

mg l^{-1} in the first flush. Peak values taken from a surface water outfall during storm events were also measured at over 7500 mg/l (SEPA, 1997). The report produced by the Forth River Purification Board (1994), found the mean concentration of suspended solids to be over five times the permissible maximum levels for treated sewage. What was described by Ellis (1979), Sartor & Boyd (1972), Bradford (1977) and, in more recent years Ball *et al.* (1998), is that contaminant constituents are more likely to be adsorbed to finer rather than larger particulates, supporting analyses that demonstrate that Cu, Pb, Mn, Zn and hydrocarbons are the major contaminant sources entering streams in association with the suspended sediment load (Hall, 1997). Instream concentrations can be exacerbated by the resuspension of previously deposited material during stormwater discharges; deemed to be the most common mechanism of contaminated sediments affecting the water column in urban streams (Field & Pitt, 1990). The composition of surface sediments in the catchment is heterogeneous, the major component being consistently found to be inorganic matter similar to sand and silt constituting up to 70% of total sediment weight. What is also clear is that the organic portion of sediment suspended in stormwater is less than that found in wastewater and comprises on average, some 20 to 40 % of the solids by weight (Ellis, 1986; Harrop, 1984). Suspended particulate matter in urban stormwater has different sizes, shapes, densities and biochemical activity consequently settling at different rates and undergoing different transformation processes.

Oxygen-demanding substances

The dissolved oxygen content of receiving waters is the most important parameter for the health of aquatic biota. Unsurprisingly therefore, dissolved oxygen suppression is reportedly the most studied urban runoff effect, (Field & Pitt, 1990), with extensive literature available on dissolved oxygen suppression as a consequence of urban stormwater runoff, e.g. (Hvitved-Jacobsen & Harremöes, 1982; Huber, 1986; Jubb *et al.*, 1998; Harremöes *et al.*, 1996). Many of the problems associated with water quality are due to the presence of organic matter. Simply, the higher the biochemical oxygen demand (BOD), the more organic matter there is in the receiving water, with aerobic digestion of organic matter by bacteria depleting the dissolved oxygen (DO) available. In the absence of oxygen, anaerobic digestion takes place resulting in unstable products such as methane and hydrogen sulphide. BOD levels in

stormwater in excess of 100mg/l have been reported in the literature, (Wilkinson, 1955; Cordery, 1976 cited in Harrop, 1984). Soluble and fine particulate organics exert an immediate DO depletion, which can be exacerbated by the resuspension of benthic material that accumulates at the bottom of a watercourse. Normally these solids exert a delayed DO demand. Typical undisturbed sediment oxygen demand levels vary between 0.15 and 2.75 $g\ m^2\ d^{-1}$, accounting for a permanent deficit of about 1.5-2.5 mg/l in the DO regime of the receiving water (Ellis & Hvitved-Jacobsen, 1996). DO balance can be further exacerbated during storm events by elevated instream chemical oxygen demand (COD) and NH_3-N concentrations following dilution and mixing with even minor runoff events causing elevated levels (House *et al.*, 1993).

Heavy metals

Heavy metals are ubiquitous, toxic and persistent in the environment. They are of significant interest in the field of urban stormwater management not least because of their detriment to the ecological health of receiving waters. Davis *et al.* (2001), indicated the ranges for the four most common heavy metals: Zinc (20- 50,000 $\mu g\ l^{-1}$), Copper & Lead (5 - 200 $\mu g\ l^{-1}$) and Cadmium (< 12 $\mu g\ l^{-1}$), and this is supported by Garnaud et al., 1999) both from their presentation of mean values gleaned from the literature and their own studies in France. Research has shown that metallic micropollutants are mainly linked to finer sediments (Ellis & Revitt, 1982), with Ellis (1979) demonstrating that although only 4-8% of surface particulates are less than 60 microns in size, they account for 30% of heavy metals. The particulates with the highest concentrations are usually associated with street surfaces and car parks and as such, several studies have observed "substantial sediment heavy metal enrichment in urban receiving waters" (Herricks, 1995). Unsurprisingly, just as heavy metal concentrations increase with decreasing surface particulate size, the same has been found to be true of receiving water sediments (Wilber and Hunter, cited in Herricks, 1995).

Toxic organics - e.g. pesticides, PCBs

An extensive range of manufactured organic chemicals is now noted to be detrimental to the health of many organisms. Pesticides such as DDT were used extensively and effectively in the 1950's and 1960's to control the *Anopheles* mosquito as well as in agriculture. However, it is persistent in the environment and although relatively insoluble in water is readily soluble in fats and oils, bioaccumulating in fatty tissues of many organisms. Monitoring programmes of pesticides in the U.S. and Canada have detected the widespread occurrence of DDT in natural waters and sediments (Gillis *et al.*, 1995).

Polychlorinated biphenyls (PCBs) are common in the environment and were extensively used for benign purposes such as heat exchanger fluids and as a plasticising agent in rubber products. They are highly stable and persistent in the environment and an indicated carcinogen. The paper by Walker *et al.* (1999), suggested that in addition to being a significant contributor of heavy metals, urban runoff contributes significant quantities of high molecular weight PAHs, PCBs and DDT. Estimates also demonstrated that urban runoff accounted for a significant contribution to the aforementioned contaminants in river sediments. A review of five studies into urban runoff and contaminant loading can be found in the paper by Walker *et al.*, (ibid.).

Inorganic nutrients - nitrogen, phosphorus

Inorganic nutrients such as nitrates and phosphates promote plant and algal growth, impacting on the dissolved oxygen balance of the water by increasing the oxygen demand via respiration of algal and macrophytic biomass, and by the oxygen demand of decomposing dead algal biomass. According to Henry & Heinke (1989) concentrations as low as 0.01 mg l^{-1} for phosphorus and 0.1 mg l^{-1} for nitrogen may be sufficient for eutrophication (nutrient enrichment) when other elements are in excess and a stream may be considered eutrophic when its algal biomass concentration is between 350 and 500 mg l^{-1} (Žáková, cited in Novotny & Olem, 1994). Mean annual loads are however, an order of magnitude less than those from secondary treatment plants and benthal sediments act as efficient sinks for both phosphorus and nitrogen, (Hvitved-Jacobsen 1982; Malmqvist 1986).

Bacteria and viruses

Urban runoff can contain a range of bacteria, viruses and pathogens. A report by Olivieri *et al.* (1977), found coliforms, pathogens and viruses in both combined and storm sewer flows. The ranges of faecal coliforms in storm runoff were between 200 and 2000 MPN per 100 ml, with the majority of samples containing >2000 MPN per 100ml. Outfalls discharging surface water have been found that equate to as little as 1 : 1 dilution of untreated sewage; >500,000 faecal coliforms per 100ml, (SEPA, 1997), probably indicating the typical problem of miss-connections to foul drains, wrongly plumbed toilets and to a lesser extent animal excreta in surface deposits. A Water Research Centre study, conducted on behalf of the NRA, concluded that an average daily rainfall in excess of 0.3 mm will generate a faecal coliform load equivalent to treated sewage effluent.

Petroleum - based substances or hydrocarbons

Typically petrol is composed of various hydrocarbons - the main compounds are alkanes, monocycloalkanes, dicycloalkanes, akylbenzenes, indanes, tetralins, naphthalenes and some oxygenated alcohol additives (Christenson & Elton, 1996). All the compounds are acutely toxic and have noticeable health effects at high concentrations. Of the alkylbenzines, benzene is a known carcinogen. In studies by Hoffman (1984), urban runoff was been found to be the source of 48% of the petroleum hydrocarbons entering the receiving water, with annual loadings from residential areas measured at 180 kg km^2. Paul & Meyer (2001), report that petroleum-based compounds are frequently to be found in stream sediments at concentrations that are stressful to sensitive stream organisms. Evaluation of study observations by Shepp (1996), suggested that runoff concentrations of petroleum hydrocarbons from land with heavy vehicle usage typically range from 0.7 to 6.6 milligrams per litre, although levels as high as 30 mg/l have been reported (NRDC, 2001). The measured and visual observations gathered throughout the course of the study suggested, with the notable exception of expensive, new cars, virtually all motorised vehicles seep a measurable volume of petroleum hydrocarbon based lubricating agents, in addition to accidental and deliberate spills of engine oil and petroleum based products.

Acids

In natural waters, carbon dioxide from the atmosphere and from bacterial oxidation of organic matter and mineral acidity from industrial wastes, mine drainage and from acid rain, are the principal sources of acidity. Acid Deposition results from either dry deposition (gases and dry particles) or acid precipitation from sulphur dioxide (SO_2) and nitrogen oxides (NOx). Atmospheric SO_2 and NOx come from burning fossil fuels, mainly coal and petroleum, from both stationary and mobile sources. These pollutants mix with water vapour, forming sulphuric and nitric acids that affect ecosystems.

Humic substances

Humic substances are formed by the biochemical transformation of plant and animal residue, and constitute a major fraction of the dissolved and particulate organic matter in natural ecosystems. They are ubiquitous in the environment and provide multiple sites for chemical reaction, making them relevant to processes such as mineral weathering, nutrient bioavailability, and contaminant transport. According to Davis & Ghabbour (2001), aquatic scientists now realise that they may constitute as much as 95% of the total dissolved organic matter in aquatic systems. They are related to a wide variety of water quality problems and are related to health risks because they react with chlorine to form chlorinated hydrocarbons, which are considered to be carcinogenic. They can increase the bioavailability of toxic metals and micronutrients, or conversely they can sequester toxic compounds, thus reducing their toxicity. Additionally, they can be available as a food source for micro-organisms, which can lead to the development of biofilm on surfaces, causing the problem called biofouling (Buhs, 2000), as well as an increase in dissolved oxygen depletion.

Thermal enrichment

Many impervious areas synonymous with the urban environment such as asphalt roads, car parks, pavements and roofs are known to transfer thermal energy to urban stormwater as it runs over these surfaces which can subsequently have severe impacts on receiving waters (Schueler, 1987), such as increased E-Coli levels.

Research by Van-Buren *et al.* (1999), noted an outfall discharge of 23^0C compared to an average upstream catchment runoff of 21.3^0C. Of more interest perhaps was the decrease in temperature from 24.9^0C from Van Buren's asphalt test plot and the outfall, attributed to cooling off during flow through the drains. Of note, is the effect of generally increasing metal toxicity as water temperature increases due to accelerated chemical activity and metabolism of affected organisms. Biological oxygen demand is also increased with temperature elevation acting as a catalyst.

2.4 Sources of contaminants in urban stormwater

Individual sources of pollution contained in urban stormwater are described in various texts by (Burton & Pitt, 2002; Ellis 1986; James & Boregowda, 1986 and Novotny & Chesters, 1981). But, as Novotny & Olem (1994) point out, it is not the land that produces pollutant loadings, but inputs, processes and activities that occur on the land. Runoff contaminants originate from activities on the land, 'dryfall' and 'wetfall' atmospheric deposition and exchange of groundwaters and surface waters. A list of these processes and inputs are, after Novotny & Olem (1994):

- pollution contained in precipitation;
- erosion of pervious lands;
- accumulation of dry atmospheric deposits (dust) and street dirt, and subsequent washoff from impervious surfaces which originate from: street litter, dust and dirt, vehicular emissions and organic residues from vegetation and animals;
- corrosion of vehicle parts and construction materials such as roofing and guttering;
- solids accumulation and growth in drains;
- leaching of contaminants from septic systems and other sources onto surfaces and into groundwater and subsequently into storm drainage;
- application, storage and washoff of de-icing and other chemicals;
- application of pesticides and fertilisers onto grassed urban lands;
- discharge of contaminants such as engine oil, brake fluid, detergents and other household solvents and chemicals;
- cross-connections of sewage and industrial wastes from sanitary sewers, septic tanks and other sources.

2.5 Pollution Input Processes

Atmospheric deposition of contaminants is typically divided into wet and dry surface loading. Atmospheric loading with contaminants has been long recognised despite statements by the likes of Mische & Dharmadhikari (cited in Harrop, 1984), that 'rainfall....could be assumed relatively pure'; the effects of 'acid rain' being a simple example to the contrary that is familiar to most people. As Ellis (1989a) highlights, in regions typified by acid rainfall, wet deposition is an important source of freely dissolved species which will be further enriched by leaching and solubilisation of the exchangeable fraction contained within impermeable surface dusts. Precipitation is extremely efficient at scavenging a range of contaminants and in quantities that can be harmful to receiving water ecosystems, although dry deposition; removal from the air by gravitational settling, surface impaction and electrostatic attraction for example is, according to Novotny and Olem (1994), probably much greater than wet deposition in and near urban areas. Ellis (1989) states that dry fallout is a relatively minor component with wet deposition predominating, accounting for a wet : total deposition ratio of about 60-70% for most pollutants. The predominant atmospheric effects of urbanisation is the chemical alteration of the atmosphere through the release of compounds such as nitrogen oxides, CO_2, sulphur compounds such as SO_2, SO_3 and H_2SO_4, largely derived from the combustion of coals and oils. The sources for these contaminants include industrial processes, incinerators, sewage treatment works and typically; vehicular emissions, released either in gaseous or solid form. Particulate aerosols in the atmosphere also contain appreciable quantities of toxic metals, pesticides, toxic organics, fungi, pollen, soil, nutrients, tars and a variety of compounds such as chlorides, fluorides, fluorocarbons and ozone (Novotny & Olem, 1994). In a study by Marsalek 1989 (cited in Walker *et al.* 1999), up to 89% of the PCB loadings to Lake Superior were estimated to have originated from atmospheric deposition. The majority of PAHs, are reported to originate from combustion sources, including the burning of fossil fuels (Walker *et al.*, ibid.).

Clearly, the greatest sink for the above pollutants are impervious surfaces such as roads and roofs. Davis *et al.* (2000) found that in addition, roofs and building walls themselves were a significant source of the metals cadmium, copper, lead and zinc in

surface water runoff. Förster (1996) in his study of roof runoff contamination, found that metal surfaces on roofs caused runoff pollution which was extreme in the case of zinc clad roofing. A list of constituents in runoff from road surfaces (table 2.1, overleaf), illustrates the primary sources of these contaminants. Coupled with the fact that "almost all street refuse can be found within 1 metre of the kerb" (Novotny & Olem, 1994), has led to the widespread interest in street sweeping as a measure for reducing the volumes of contaminants contained in urban stormwater. However, Terstrep *et al.* (1986) stated that street sweeping will not generally improve water quality, probably because although sweeping is effective in removing litter and coarse particulates, the efficiency decreases with particle size (Sartor & Boyd, 1972). Bender & Terstrep (1984) concluded that sweeping is ineffective for particles $< 250\ \mu m\ \varnothing$ and yet it is this fraction which is closely allied to metallic micropollutants (Ellis & Revitt, 1982; Grottker, 1987). Similarly, in a study by Gromaire *et al.*, (2000), street washing was found to be similarly limited for removal of heavy metals and that with the exception of organic particles, the fraction of fine particles removed by street washing was far smaller than that which is removed during a rainfall event. A further difficulty, as Harrop (1984) points out, is that to separate one particular road from an entire urban environment in order to identify its particular sources of contaminants, (as has been done in a number of studies) invokes serious problems. This is important in identifying those pollutant sources that are either entirely, or to some considerable degree, associated with the road surface itself.

Constituents	Primary sources
Particulate	Pavement wear, vehicles, atmosphere, maintenance
Nitrogen, phosphorous	Atmosphere, roadside fertiliser application
Lead	Auto exhaust, tyre wear, lubricating oil and grease, bearing wear
Zinc	Tyre wear, motor oil, grease
Iron	Auto rust, steel highway structures, moving engine parts
Copper	Metal plating, bearing and brushing wear, moving engine parts, brake lining wear, fungicides and insecticides
Cadmium	Tyre wear, insecticide application
Chromium	Metal plating, moving parts, brake lining wear
Nickel	Diesel fuel and petrol exhaust, lubricating oil, metal plating, bushing wear, brake lining wear, asphalt paving
Manganese	Moving engine parts
Cyanide	De-icing compounds
Sodium/calcium chloride	De-icing salts
Sulphate	Roadway beds, fuels, de-icing salts
Petroleum	Spills, leaks or blow-by of motor lubricants, anti-freeze and hydraulic fluids, asphalt surface leachate
PCB	Background atmospheric deposition, PCB catalyst in synthetic tyres, spraying of road markings

Table 2.1: Pollutant constituents in runoff from road surfaces after (Ball *et al.* 1998)

2.6 First flush

The first flush effect concentrates pollutant loads in the first part of runoff waters and is a significant feature in some systems. Typically, in urban areas, sediments and pollutants accumulate during the antecedent dry weather period to be transported by effective rainfall to the receiving waters, with a greater mass of pollutants in the early stages of the flow. Work by Ellis (1976) and Mance & Harman (1978) confirmed the phenomenon in this respect, however the first flush is not easily quantified, and much variation has been noted dependant on rainfall-runoff lag times, effective rainfall, sediment size, intake line velocity and antecedent dry period.

Studies into surface water discharges such as those by Wilkinson (1955) have

noted a large variation in the contaminant loads which is not always consistent with the theory that pollutant load reduces with time of discharge, or for that matter with length of the antecedent dry period. Grottker (1987) for example, has shown that because larger particles are removed more efficiently, heavy metal concentrations are consequently higher after a rainfall event than before. Deletic (1998), concluded from her study that there is usually enough pollution available for wash-off to continue during the entire duration of ordinary storm events, meaning that the occurrence of a first flush is more likely to be associated with large and intense events. Deletic also concluded that the phenomenon was site specific.

Because for practical purposes there is a need to understand which portion of the discharge is most polluted, and therefore by inference that which may require treatment or detention, a clear definition of the phenomenon has been attempted by the likes of Saget *et al.* (1996) and Bertrand-Krajewski *et al.* (1998). Their studies concluded that the first flush was significant if 80% of the total mass was transported in the first 30% of the volume of run off. In terms of separate sewer systems, Bertrand-Krajewski deduced that for 50% of rainfall events, 50% of the total pollutant mass is transported in the first 38% of the total volume and 80% of the total pollutant mass is transported in the first 74% of the total volume.

2.7 Urbanised streams

Papers by Wilkinson, 1955; Ellis, 1979; Shutes, 1984; Harrop, 1984; Payne & Hedges, 1990; Seager & Abrahams, 1990; Harremöes *et al.*, 1996; Hall, 1997 and Faulkner *et al.* 2000, have considered the impact of stormwater discharges to urban watercourses in site specific studies. However, in all but that conducted by Ellis (1979), Shutes (1984) and Wilkinson (1955), results appear to have been mitigated by the presence of point sources of pollution such as Combined Sewer Overflows (CSOs), miss-connections to foul sewers and pollution incidents (Payne & Hedges, 1990).

The difficulty, as Field & Turkeltaub (1981) have suggested, albeit in relation to ascertaining dissolved oxygen impacts, is that it is difficult to locate urban areas free from all interference except urban runoff. Davis & George (1987) conducted a study into the spatial differences in macroinvertebrate communities along the River Roding in Essex. They found that whilst invertebrate community structure could be

explained largely in terms of organic enrichment (e.g. from CSOs and inputs of piggery waste), the effects of metals were masked by the more obvious effects of organic enrichment. Similarly, Huber (1986) observed that expected water quality impacts from urban runoff are subtle and often masked by the effects of sewage effluents or industrial waste. Even so, definitive evaluation of the impacts of urban stormwater on receiving waters is bedevilled by the extreme variability and inconsistency of urban stormwater data. This is reported in a large number of field investigations (Brinkmann, 1985), and echoed by the likes of Field & Pitt (1990), who point to the specificity of each individual catchments' characteristics.

The benchmark study Wilkinson, conducted back in 1955, was in response to misgivings at the time that although many advantages were being claimed for the use of separate drainage systems in new housing developments, possible pollution of streams was being caused by the first flush phenomenon. Wilkinson concluded that there was indeed, in many cases, a first flush of water, which was more polluting than the rest of the storm. Several exceptions were noted though, e.g. water discharged throughout some storms was more polluting than the 'first flush'' of other storms. In terms of Biochemical Oxygen Demand, it was concluded that diverting surface waters to the stream rather than to combined sewers reduced the pollutant load in the receiving waters. In terms of suspended solids it was noted that the load probably increased by six to seven times and although settling tanks or lagoons were mooted as being useful in reducing the weight of discharged solids, it was concluded that other than that, there was little advantage in subjecting the runoff to treatment. Acknowledgement was made by Wilkinson of the potential effects commensurate with lower volumes of water to dilute the first flush in smaller catchments. The receiving water for his catchment is the River Hartsbourne, a tributary of the Colne; both classified rivers. Research since 1955 has revealed stormwater to be far less innocuous than originally thought, although it must be stated that population, building developments and car ownership have all increased dramatically since the 1950s.

Ellis (1979) in a study on the separately sewered Graham Park catchment in London, considered the quality of an urban stormwater discharge to the Silk Stream, a tributary of the River Brent. The study considered the composition and associated biochemical quality of sediment discharged from a single culvert outfall. It was concluded that pulse loadings of particulates to streams during storm events were often of raw sewage quality and that the relationship between sediment discharge and

stormwater flow could be highly variable. Although the biology of the river was not determined, it was suggested that although urban runoff does not maintain a high loading for prolonged periods, the impact of the pulse would impart a permanent deficit to the habitat and ecological balance. Later work by Ellis (1986), showed that sediment accumulation of pesticides, nutrients, hydrocarbons and metals made their toxic effects available over time. Similarly, Harrop (1984), investigated the quantity and quality of discharge from a flume, used to convey the surface water runoff from a 274 hectare housing estate in Watford. Typical flows were reported as being in the region of 0.7 - 2.7 l s^{-1}, with appreciable discharges only occurring during storms, producing a wide variation in receiving water quality.

Shutes (1984) determined biological scores and a range of physico-chemical parameters along the Silk Stream and its tributary, the Dean's Brook, from its 'semi-rural' source to its urbanised section, below the Graham park outfall studied by Ellis (1979). The study indicated that a substantial proportion of the hydrocarbons associated with benthal sediments were derived from storm runoff from road surfaces. Possibly due to the extensive modification of the watercourse, biological assemblage was poor with a complete absence of stoneflies and mayflies and only one family of caddis fly at the most upstream site. Of significant interest was the marked decline in species richness from upstream to downstream, despite the absence of sensitive species.

Payne (1989), in her study of forty-seven individual surface water sewers, came to the broad conclusion that reduction in biological diversity increases with the area of the sewered catchment and that impacts are more likely to occur downstream of outfalls fed by catchments (i.e. sewered area) over 50 hectares, with residential areas having the least impact. Payne suggested that the greatest score reductions occur where the initial water quality is highest, although biotic scores were limited to those used in assessing the effects of organic pollution. However, no attempt was made to measure the quantity or quality of discharges or the cumulative impact of successive outfalls on a sub-catchment level.

In greater focus, numerous studies have concentrated on the potential impact to watercourses directly from road runoff (Perdikaki & Mason, 1999; Maltby *et al.*, 1995a, 1995b; Beasley & Kneale, 2002, 2003; Boxall & Maltby, 1997). The study by Maltby *et al.*, (1995a), demonstrated that there was an increase in the sediment concentrations of total hydrocarbons, aromatic hydrocarbons, and heavy metals and

an increase in the water concentrations of heavy metal and selected anions downstream of motorway runoff discharges. In four out of the seven sites surveyed, differences between the stations upstream and downstream of discharges were noted, although in only one case was there a significant difference in macroinvertebrate assemblage. Although the quality of receiving water and sediment was altered a short distance from inputs of motorway runoff, observed toxicity was experimentally determined as being due to PAHs (Maltby *et al.*, 1995b). Subsequent tests indicated that pyrene, fluoranthene and phenanthrene were responsible for the toxicity of the sediment extract (Boxall & Maltby, 1997).

Industrial areas and motorway runoff depress macroinvertebrate numbers but according to Beasley & Kneale (2002), drainage from streets with no off-road parking in residential areas can have similar impacts. Their results showed that it was not always the metals and PAHs with the greatest total concentrations that were causing ecological damage, concluding that Ni and Zn were the critical metals, whilst benzo(b)fluoranthene, anthracene and fluoranthene were the most contaminating PAHs. An important point raised by Beasley & Kneale is that generally whilst increasing urbanisation and road construction means that heavy metals derived from nonpoint sources are likely to cause further impairment of stream ecology, current knowledge of metal contamination is related primarily to point and downstream measurements form known sources. For example, Coimbra *et al.,* (1996), who assessed macroinvertebrates and physico-chemical parameters downstream of an industrial point source discharge. Beasley & Kneale (2003), identified zinc and nickel within stream sediments as the main metal influences, with analyses confirming the established results of Clements (1994) and others, that Ephemeroptera are particularly sensitive to metals. However, 76 % of the variation in assemblage was not explained by the presence of metals, possibly suggesting the presence of other contaminants.

Perdikaki & Mason (1999) studied invertebrates and metals in sediment and invertebrate body tissue at nine points above and below crossings of major trunk roads. The study concluded that there was no major impact on the macroinvertebrate communities due to road runoff at the study sites because neither the sediments nor macroinvertebrates had consistently higher amounts of metals at the downstream sites.

2.8 The importance of small urbanised streams

Although the effects of stormwater associated with CSO discharges and highway runoff have been widely studied (Seager & Abrahams, 1990; Maltby *et al.* 1995; Wagner & Geiger, 1996; Perdikaki & Mason, 1999; Sriyaraj & Shutes, 2001), few investigations have concentrated on surface water outfalls in isolation and their biological and chemical impact on small urbanised streams. Charlton Brook, the focus of this study is one of these typically unclassified rivers. Total river length in England & Wales is estimated to be between 95,000 and 130,000 km (Furse, 1997) of which, the majority do not receive classification and therefore are not subject to the routine Environment Agency General Quality Assessments (GQA).

Presently, watercourses are not classified if their 'natural summer flow' is less than $0.3m^3/s$. As such; they presently do not receive classification under the Environment Agency's General Quality Assessment, (Robins, 2001; Environment Agency, 1997). River quality monitoring excludes the smallest streams with catchments <10 km^2, except where they are the main source of a larger river, or are substantially polluted. This is in accordance with European conventions, and avoids having to monitor small streams which may seasonally dry up (SEPA, 2004).

However, one of the principal environmental objectives of the EC Water Framework Directive; Article 4, is to ensure achievement and maintenance of 'good status' for all Community waters by 2015 (2000/60/EC); rather than "those that member states choose to designate" (DETR, 2001). Interestingly, the Scottish Environmental Protection Agency intends to reduce the number of unclassified rivers to near zero by the time the EU water Framework Directive systems are in place in 2006, through an extension of ecological quality monitoring sites (SEPA, 2004).

The size of water bodies is not strictly defined in the WFD, being described as 'a discrete and significant element of surface water such as a lake, a reservoir, a stream, river or canal, part of a stream, river or canal, a transitional water or a stretch of coastal water' (2000/60/EC, Article 2. Para. 10). Consequently, Governments could possibly continue to ignore smaller water bodies, such as ponds, small streams, ditches and the like. Indeed, the Environment Agency considers that many of the small stream that have catchments smaller than the 10 km threshold mentioned above, will not represent what they term 'significant management units to warrant identification as water bodies' (E.A. 2002). Presumably, this is at least partially due,

to the assertion that many [small streams] will be adequately managed by being included in an appropriate larger water body (E.A. ibid.).

Yet, whilst the proportion of unclassified watercourses receiving discharges from urbanised catchments is unknown, due to housing growth, it is estimated that the urban area of England alone will increase from the 10.6 % existing in 1991 to 11.9 % by 2016 (Housebuilders Federation, 2002). Although the Review of the Building Regulations, 1991 (Part H), encourages the use of sustainable urban drainage systems, use of SWOs may still occur depending on site conditions, possibly continuing to be the preferred option, resulting in a further deterioration of in-stream quality over this period, without widening statutory control.

Unlike CSOs, stormwater discharges from separately sewered catchments are not routinely regulated in the UK. The control of point source discharges such as CSOs is relatively straightforward in comparison to diffuse sources. For example, the focus of the AMP 3 Periodic Review (2000-2005), is a reduction in the number of unsatisfactory CSO discharges to improve amenity, aquatic life and bathing standards; supporting the view that the frequency or volume of such discharges is a good indicator of the pollutant impact on receiving waters (Lau *et al.*, 2002). In pursuance of the AMP 4 Periodic Review (2005 - 2010), the setting and achievement of River Quality Objectives for smaller (unclassified) rivers for the control of sewage is anticipated, adding these to the national set of RQOs (Warn, 2002). Despite this, contamination of surface waters is unlikely to improve, with vehicular induced pollution likely to increase as traffic volumes are forecast to grow from 488 billion vehicle km in 2000 to 688 billion vehicle km a year in 2025 in the UK (Transport Research Laboratory, 2002). Surface water impacts to unclassified watercourses may also increase in severity and extent in the future due to the projected increases in urban housing developments, potentially requiring their consideration as point source discharges to classified rivers.

Analysis of the literature by Furse (1998) states that there are some 183,000 first and second order streams within the UK, with the suggestion that they account for more than 50 % of the total length of British streams and rivers. Despite the abundance of small streams, studies of their stream fauna are comparatively rare, but have suggested that headwater streams make a significant contribution to the species pool of a catchment (Furse, ibid). Despite this, small urban watercourses by their very nature tend to be ignored by regulatory bodies, with headwaters (defined as a

watercourse within 2.5 km of its furthest source; Furse, 2000) comprising only 12 % of GQA sites (Furse, ibid.). However, their importance as ecological and amenity resources should not be overlooked. Such sites serve as valuable green corridors in that they form an integral part of the network linking urban areas to the wider countryside.

The UK biodiversity Action Plan (UK Biodiversity Partnership, 1994) defines four categories of green space, one of which is 'remnants of ancient natural systems, such as woodland, wetland, freshwater and estuarine'. It is this type of habitat, such as Charlton Brook, that give bats, kestrels, great crested newts and rare species such as ground nesting bees the mixture of breeding, foraging and sheltering areas they need (Lloyd, 1999). As rural habitats continue to be lost and fragmented, urban areas are becoming increasingly important for biodiversity. Most urban areas in fact support a higher diversity of wild species per unit area than intensively farmed countryside. Urban nature reserves and other wild green spaces provide the only local contact with nature for the 80% of the population living in urban areas, and offer a wealth of educational, economic and social benefits (UK Biodiversity Partnership, 1994). As Paul & Meyer (2001) have stated, most humans will continue to live in cities in the future and hence, urban areas lie at the intersection of human and ecological systems, concluding that; if we are to succeed in the oft-stated goal of incorporating humans as components of ecosystems, cities and their streams can no longer be ignored. This is especially pertinent if one considers that by 2025, it has been estimated that the worldwide urban city population will number 5.5 billion people, with 400 cities having a population of over 1 million people (Roesner, 1999).

The EC Water Framework Directive (2000/60/EC) has placed catchment management at the centre of European water protection policy by requiring Member States to maintain the ecological quality of all fresh waters in a catchment context (Williams *et al.* 2003). This sustainable management requires, inter alia, knowledge of the biodiversity characteristics and importance of different water body types within catchments (Schneiders & Verheyen, 1998 in Williams *et al.*, ibid). For unclassified watercourses, this is in clear contrast to the status afforded them by regulatory bodies in monitoring and protection strategies. Ensuring that biodiversity loss can be avoided within catchments requires a ... monitoring approach that encompasses small sites... (Williams *et al.*, 2003). Under the Water Framework Directive, there is also the requirement to characterize pressures and impacts on the water environment and a

better understanding of the causes and characteristics of urban pollution is needed (Wilson *et al.*, 2003).

2.9 Techniques and procedures pertinent to the study

Biomonitoring of urban catchments suggests that the magnitude of concentration and loadings associated with urban runoff is sufficient to provide the critical limiting factor for receiving water ecology (House *et al.*, 1993) with studies suggesting that biological sampling implies a lower quality classification than that derived from chemical sampling (Faulkner *et al.*, 2000; Cessford, 1997). By the same token, a number of authors have recognised the need to integrate biological and chemical assessment (Burton & Pitt, 2002; Ellis, 1991; Green & Faulkner, 2000) given its greater accuracy in assessing the quality of watercourses. This need is now recognised internationally at least in so far as the Water Framework Directive requires that good ecological status should be achieved for water bodies by 2015. Status is determined on the basis of ecology because the Directive requires that quality is determined not just by the chemical composition of waters but by the fish, plant and other life that inhabit it (Scottish Executive, 2004).

Biological evaluation of the study watercourse was deemed an essential part of the study. The River Invertebrate Prediction and Classification Scheme (RIVPACS) was identified for this purpose. RIVPACS is a software package in common use with the Environment Agency and the Scottish Environmental Protection Agency in environmental assessment, typically in measuring the effects of river regulation on faunal communities (Beech, 2001). Its utility lies in measuring the quality of assemblages in terms of the similarity between taxa present at a site with those that would be expected in the absence of pollution. However its application to small streams such as Charlton Brook does pose a practical difficulty, with the characteristics of small streams not according with sites used in compiling the reference database for RIVPACS. The suite of reference sites ranged from mid-sized to large streams and rivers, but excluded small streams (Clarke *et al.*, 2003). The inclusion of small streams is under review, but the version used in the study (RIVPACS III), which generally excludes them, is still used by government agencies as the principle tool for assessing the ecological quality of rivers in the UK. RIVPACS predictions were therefore utilised in this study as they form the basis for

Environment Agency grading of biological quality. Limitations in the use of RIVPACS also extend to its derivative indices, based on implied tolerance to organic pollution. These are the Biological Monitoring Working Party (BMWP) score and the Average Score Per Taxon (ASPT). Although their use is in keeping with EA methodologies, other biotic indices were incorporated into the study given the potential impact on diversity from non-organic pollution. Additionally, the GQA system is delimited by the use of the BMWP taxa only, whereas other diversity indices can incorporate all taxa found within a community. According to Yoccoz *et al.*, (2001), ecologists have developed an almost endless number of diversity indices, but most of them can be seen as weighted sums of the relative abundance of species. Ecological theory was beyond the scope of this thesis, but literature suggests that the Shannon-Weiner and Simpson diversity indices are amongst the most widely used by ecologists (Ricklefs & Miller, 2000; Ludwig & Reynolds, 1988). Work by Mouillot & Leprêtre, (1999), suggests that the indices chosen both had merits in relation to low (10 - 25) species numbers (Shannon-Weiner diversity index) and relatively small sample sizes of < 1000 individuals in the case of Simpson's diversity index Similarly, Pielou's measure of evenness was found to be reliable for 'small' sample sizes.

Sediments act as both sinks and sources of pollutants, and are indicated as the cause of beneficial use impairments (Burton & Pitt, 2002; Crunkilton *et al.*, 1996; Ellis, 1986), with the accumulation of contaminated streambed sediments argued to be the principle underlying reason for reduced biointegrity (Beasley & Kneale, 2004). This is in sharp contrast to the conclusion of Terstrep *et al.*, (1986), that very little was known (then) about the effects that pollutant enriched sediments had on aquatic life at the site of deposition or on the uses of the water body. Work by Maltby et al., (1995b) on sediments contaminated by motorway runoff concluded that most of the sediment toxicity could be attributed to hydrocarbons, of which PAHs were probably the most important. In a survey of Scottish urban rivers (Wilson *et al.*, 2003), four out of the nine streams surveyed were sufficiently contaminated that had their sediments been dredged, they would be classified as special waste in the UK. The main contaminants were found to be hydrocarbons and to a lesser extent, heavy metals associated with road runoff. Consequently, sediments were targeted as potential problem sources during this study with sediments from the brook sampled and analysed for metals and polycyclic aromatic hydrocarbons (PAHs).

Ecological responses to metals include reduced abundancies, altered community structure (Rauch & Morrison, 1999), behaviour (Kedwards *et al.*, 1996) and retarded growth (Maund *et al.*, 1992). Invertebrate uptake of metals seems to occur via direct exposure to dissolved metals and ingestion of metals adsorbed to fine particulate matter and organic matter (Paul & Meyer, 2001), leading some researchers to suggest that metal toxicity is more strongly exerted through the river bed than from the overlying water (Medeiros *et al.*, 1983; House *et al.*, 1993). Crunkilton *et al.*, (1996) highlighted the importance of chronic toxicity to stream dwelling invertebrates, suggesting a mechanism whereby urban runoff delivers contaminants to the stream channel with toxic effects being manifest during low flow conditions. Burton & Pitt (2002) have also stated that dissolved metal species accumulate in interstitial water, bacteria, macrophytes and other food chain components resulting in long-term and repeated exposures with a variety of adverse effects including increased mortality. Studies such as that by Malmqvist & Hoffsten (1999) on macroinvertebrate assemblages exposed to low concentrations of instream metals from old mining sites, support this assertion, noting reduced taxonomic richness as a consequence of water column metal pollution. This structuring of invertebrate communities was also reported in another large-scale study by Clements *et al.*, (2000). Much work has been done on the effect of particular metals to invertebrates and fish, typically determined by laboratory based tests such as the LC 50, and one consequence of this has been the derivation of standards for the protection of aquatic life (U.S. EPA, 1986; CCME, 1998). However, because of the complex interactions between different pollutants and their exposure to aquatic organisms it is difficult to ascertain which substances are contributing to toxicity (Crunkilton *et al.*, 1996). This is compounded by the typically sub-lethal levels of individual pollutants within watercourses.

Work by Spehar & Fiandt (1986) and Enserink *et al.* (1991) showed additive effects of metals at chronic concentrations, leading Clements *et al.* (2000) to develop a measure of toxicity based on the additivity of metals as a proportion of their water quality guidelines, defined as the Cumulative Criterion Unit (CCU). The method has been employed once in the UK by Hirst *et al.* (2002), with limited success. Their study involved the taking of a sample from fifty-one sites across Wales and Cornwall, approximating Clements' study of seventy-three individual streams. It was decided to test the methods' utility within the study site in determining whether a temporal and

spatial variation existed along the length of the watercourse, and if the results bore any relation to the macroinvertebrate assemblage.

Because admixtures of instream pollutants are unlikely to be solely comprised of metals, an additional measure of potential sediment toxicity was incorporated into the study similar to Clements' CCU approach, which combines empirically derived concentrations of pollutants with the probable effect level (PEL) thresholds defined in the Canadian Sediment Quality Guidelines for Aquatic Life. To the author's knowledge this method is untested in the UK and was similarly utilised to determine whether changes in macroinvertebrate assemblage could be indicated by the implied toxicity of the bed sediment.

It is widely understood that rain transports pollutants from both the land and the air, via drainage to receiving waters. For the purposes of the study, there was a need to determine whether the contribution to storm induced pollution within the watercourse was a consequence of runoff from the impermeable portion of the catchment. Intuitively, it was felt that the rural portion of the catchment would not be the major contributor to instream pollution during storm events, due to the flashy nature of impermeable runoff and the filtration of much rainfall falling on permeable surfaces. To determine whether pollutant loadings were associated with the urbanised catchment, hydraulic modelling was employed using Hydroworks (Wallingford Software & Anjou Recherche, 1999), converting empirically derived rainfall data into runoff for both the rural and urban areas. Empirically derived discharge data from points located at the downstream end of the urban rural sections of the catchment were then compared with the Hydroworks predictions.

2.10 Summary

Studies have considered the mass and concentration of pollutants from surface water runoff with those of sewage discharges, so the potential for harm to beneficial uses of receiving water has been widely reported. What is less well understood is the degree of impact within small urbanised streams, that typify watercourses under increasing environmental pressure, and largely ignored by the regulatory bodies. The various components of this study are generally well tested, especially the physico-chemical and biological assays. However, the holistic incorporation of the methods presented and their focus of application is not. The urbanised stream described in the

following chapters was chosen to satisfy the requirements of the study and is described in the following chapter.

Chapter 3

Background study

3.1 Introduction

As part of the background study, a site survey was carried out to gain familiarity with the site, establish safe access points for sample collection and to determine the optimum location for equipment installation.

3.2 Study site description

The study catchment comprises Charlton Brook and its tributaries which rises in Wharncliffe chase. This is a partially urbanised tributary of the Blackburn Brook in northeast Sheffield that has a catchment area of 374 hectares. The brook flows eastwards from its origin at an altitude of 230 m, joining the Blackburn Brook in Chapeltown (Ordnance Survey National Grid Reference SK 3538 9689) at an altitude of 95 m. The channel slope is 36.4 m km^{-1} determined as the average slope between two points located 10 and 85 % along the mainstream length of 3.7 km

Plate 3.1: Urbanised section of Charlton Brook (approximate National Grid Reference: SK 342 966), illustrating typical bank side vegetation on right.

(Hall *et al.*, 1993). The upstream portion of the catchment, comprising three main tributaries is predominantly rural, consisting of agricultural grassland and deciduous woodland. Downstream of their confluence, the catchment is almost entirely

urbanised. The urban portion of the brook is bordered by woodland and amenity grassland (Figure 3.1) and has been identified as a key site and strategic green link in the South Yorkshire Forest Plan (South Yorkshire Forest Partnership, 2002).

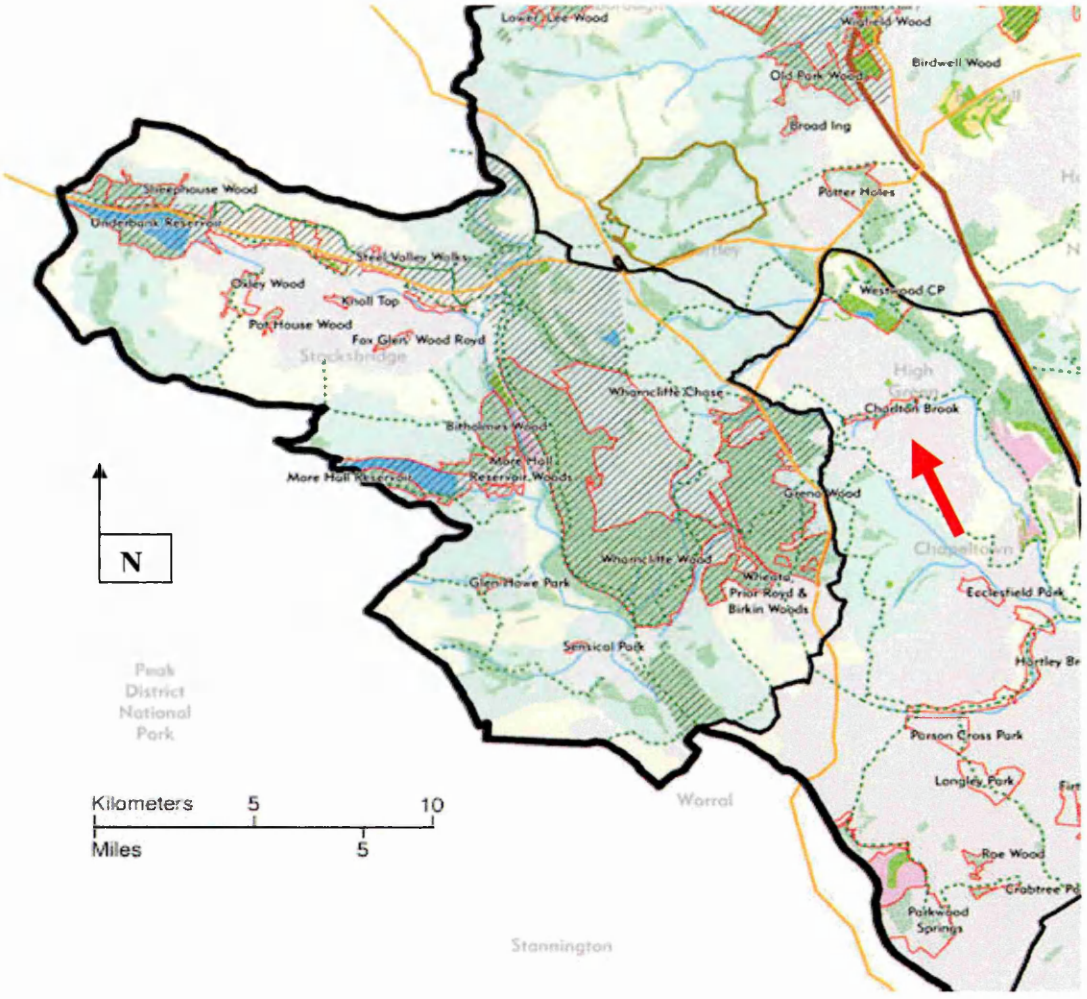


Figure 3.1: Location of Charlton Brook catchment. Source: South Yorkshire Forest Partnership, 2002.

The catchment is separately sewered and all discharges to the brook are in the form of SWOs, sixteen in all, which are located in the urban portion of the catchment (see Figure 3.2). There was evidence of a small quantity of sewer litter downstream from outfall 15 (grid ref: SK 3449 9673), suggesting some misconnection of foul drainage to this surface water drainage system. Such misuse has been reported elsewhere (Payne, 1989). The urbanised proportion of the catchment is 24.7%, comprising medium density housing including two schools; with commercial premises limited to a corner shop, garage and two public houses. The drainage

network covers 53.85 ha, or 14.4 % of the catchment, with a total impermeable area of 20.09 hectares. The impermeability of this area was calculated as 37.3 % from an average of ten representative $100m^2$ grids. Areal calculations of each drainage network were based on the network drainage map of the area supplied by Yorkshire Water (2002). The remaining urban area is not shown as contributing to the stormwater network. The population of the study catchment, based on demographic statistics (Wendell Cox, 2001) is in the region of 5,400. There have been no previous studies on Charlton Brook of which the author is aware, although the Blackburn Brook, into which Charlton Brook feeds, is subject to general Quality Assessment by the Environment Agency as part of its river quality monitoring programme.

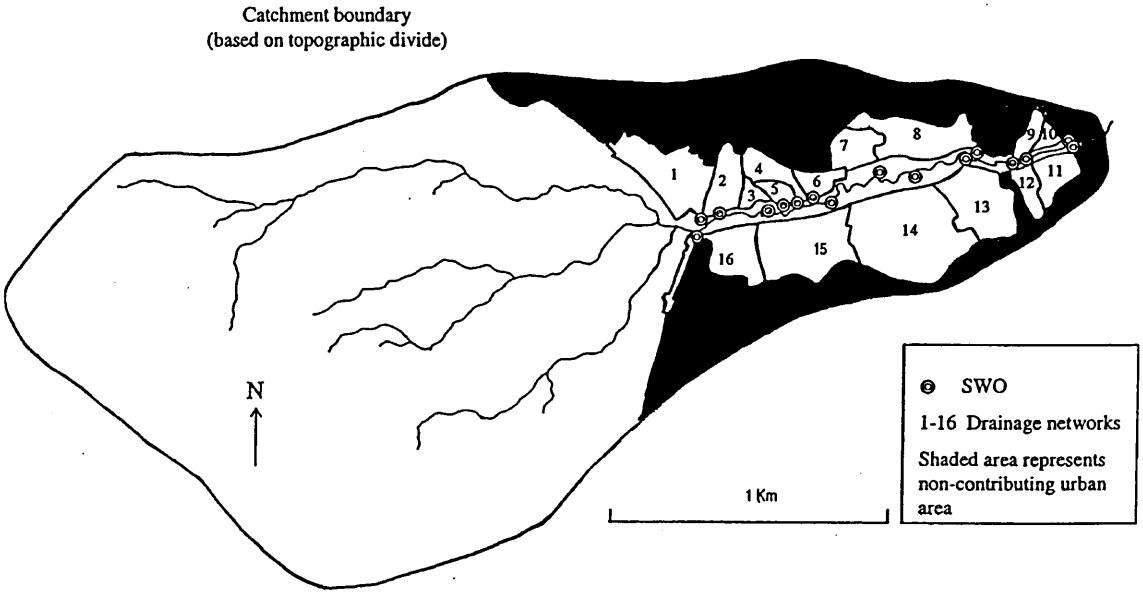


Figure 3.2: Surface water outfall and drainage network location, Charlton Brook.

3.3 Fieldwork strategy

In pursuance of the initial aims of the study (Chapter One), it was decided to undertake the following investigations:

- Perform a general quality assessment (chemistry) on the urban and rural portions of Charlton Brook, sufficient to produce thirty-six samples. Such data would enable comparison with Environment Agency figures, which are based on three years data, at a sampling frequency of once a month.

- Perform a general quality assessment (biology) along the length of the watercourse, with which to compare the results from the chemical GQA.

- Sample additional parameters in pursuance of the Urban Waste Water Treatment Directive 91/271/EEC for discharges from sewage treatment works following secondary treatment, namely COD and suspended sediment.

- Continuously record discharge at the downstream end of the catchment below all surface water outfalls discharging to the watercourse.

- Record rainfall data continuously from two sites within the catchment. Rainfall is to be recorded using two synchronised tipping bucket raingauges, one at either end of the catchment.

- Sample instream ammonia, BOD, COD, pH, suspended sediment and temperature throughout the duration of a number of storm events.

3.4 Site survey

The preliminary site visit to the urban portion of the catchment was made on 30th November, 2001. Two sites at the downstream end of the catchment were identified as suitable for positioning of hydrometric equipment; a uniform stream section (grid ref: SK 3521 9689) and the proceeding culverted stream section underneath a disused railway embankment (grid ref: SK 3523 9692).
Care was taken to ensure that sites were free from the risk of flow backing up the channel; therefore all mentioned sites have regular cross-sectional areas, can be accessed safely, and are unlikely to be unduly influenced by stream channel irregularities and blockages. The chosen sites conformed to the requirement for a

straight and uniform channel upstream, in length at least twice the maximum river width (Shaw, 1996). Two sites were also identified for the location of raingauges. Consideration was also taken into account of the likelihood of vandalism so sites were chosen with minimisation of this in mind.

Access within the urbanised section of the catchment was severely limited on certain reaches of the stream due to dense vegetation on the left bank coupled with a steep topography on the right bank. The rural portion of the catchment, whilst generally more accessible (Plate 3.2), was subject to private ownership in parts, preventing access to the lower reaches of the three tributaries. However, six sites were identified as suitable for the regular biochemical sampling. On average, EA sampling points relate to a 6 km stretch of river or canal (Environment Agency, 2003), so the method employed ensured that consequent results would be much more spatially detailed.

Plate 3.2: Rural section of Hall Wood Dyke, the uppermost tributary (approximate National Grid Reference: SK 3264 9665).

For the macroinvertebrate sampling, seven sites were chosen in order to provide a spatial comparison along the length of the watercourse, and to take account

of component tributaries, particularly Hall Wood Dyke, the northernmost stream. Additional sites were located on Blackburn Brook at points above and below Charlton Brooks' entry to Blackburn Brook for future reference. All sampling sites were chosen to be similar with respect to light and shade, substrate type, velocity, mean depth and mean width. This was to reduce the likelihood that observed differences could be attributable to riverine characteristics. As sampling was to be generally carried out by the author alone, risk assessments were carried out to ensure safety of access.

3.5 Equipment location

3.5.1 Starflow

A STARFLOW ™ ultrasonic doppler was chosen to continuously measure flow within the catchment and was installed on the 1st of March, 2002, following permission being granted by the landowners. The device was located five metres downstream of the culvert entrance (site 4; figure 3.3; plate 3.3) which was cleared of obstructions and debris prior to installation. Anecdotal evidence suggested that there was a danger of the stream spilling over its channel and onto the adjacent roadway at this point, which would nullify any measurements taken by the Starflow.

Plate 3.3: Culvert at downstream end of catchment chosen for location of STARFLOW.

Discussion with local residents however, indicate that this only occurs when debris is allowed to accumulate upstream of the culvert.

Siting ensured that the approach channel flow was straight and uniform, thus minimising, as far as possible, potential turbulence generated upstream of the culvert. A special mounting bracket was designed and produced enabling the STARFLOW to be positioned at bed dead centre, flush with the channel bed. The mounting bracket design also enabled the Starflow to be removed for routine maintenance and replaced in exactly the same position afterwards. The device was run for an initial period of five days to produce a data series for inspection and to enable assessment of its anchorage and physical effect within the watercourse. Re-inspection showed that the anchorage device appeared to be performing as anticipated with no movement having taken place within the culvert. No debris other than fine sediment had become entrained on or about the device and the sensors themselves were clear of any sediment deposits. Analysis of the data however, showed that the STARFLOW had not recorded velocities and discharge consistently over the initial period. It appeared that where higher velocities were experienced, i.e. above 0.1 m s^{-1} for a period equivalent to three logging intervals (15 minutes) discharges within ± 2% of those listed in the manually derived area rating table were produced (Appendix I). As the ultrasonic doppler requires material and / or bubbles entrained within the watercourse off which to reflect a signal, it was felt that the absence of reliable data might have been caused by the visually clean flows associated with the brook at low flow. Data logged during a storm event on the 18th March appeared to confirm this, with reasonable velocities being recorded. The aforementioned problem with discharge calculations remained however, confirming that the data logger requires a consistent velocity and depth over a number of logging intervals. Consequently the logger was updated to log with an increased frequency. In respect of low flows, it was decided to institute a series of dilution gauging exercises to establish an accurate calibration of the STARFLOW.

Although the STARFLOW can be placed in an offset position to avoid alluvial material and / or heavy debris transported during high flows, no offset programming facility exists for irregularly shaped ovoid pipes. Therefore, regular site checks to ensure that the sensors were not blocked took place in conjunction with monitoring of

logged data to indicate whether or not the sensors had become obscured, by displaying a dominance of zero signals. An alternative method is to point the STARFLOW downstream, however there was a risk that the sensor body would disturb the velocity distribution as well as introducing what the manufacturers refer to as a 'little loss of calibration accuracy' (Unidata, 2000). The non-uniform shape of the culvert required the production of a user-defined rating table from which the STARFLOW could calculate discharge based on flow cross sectional area. This is detailed in Appendix I.

Dilution gauging

In light of the STARFLOW's limitations in deriving reliable discharges for low velocities and by association, 'clear' waters, repeated dilution gauging was carried out, following permission being granted by the Environment Agency, by injection of a known volume of Rhodamine WT dye. Rhodamine WT was specifically developed for water tracing applications and is allegedly superior for quantitative work compared to its predecessors (Burton & Pitt, 2002), being easier to detect at low concentrations and less toxic. The study employed the constant rate injection method. This is defined by the British Standards Institute (1999), whereby a solution of concentration c_1 of a tracer is injected at a constant rate q into a cross-section located at the beginning of the measuring reach of the channel, in which the discharge Q, remains constant for the duration of the gauging. At a second cross-section downstream of this reach, at a sufficient distance for the injected solution to be uniformly diluted, the concentration is measured for a sufficient period of time and at a sufficient number of points to ensure that good mixing has been obtained and that the concentration of added tracer c_2 has attained a constant value.

The mass rate at which the tracer enters the test reach is:

$$qC_I \qquad (1)$$

And the rate at which the tracer leaves the test reach is:

$$(Q + q)\, C_m \qquad (2)$$

Thus: $$QC_b + qC_i = (Q + q)\, C_m \quad (3)$$

As C_b is nullified by use of actual stream water to produce C_i, and q is negligible (i.e. approximately 1 in 20,000), the following can be derived from equation 3:

$$qC_i = QC_m \quad (4)$$

$$\therefore \quad Q = q \frac{C_i}{C_m} \quad (5)$$

Where C_b = background concentration

C_i = initial concentration

C_m = measured concentration

q = initial discharge

Q = measured discharge

Mixing length was calculated using the following equation (from Herschy, 1985):

$$L = bQ^{1/3} \text{ (m)}$$

Where L = distance between injection site and sampling station (mixing length) (m)

b = 14 for mid-stream injection

b= 60 for injection from one bank

Q = stream discharge (m^3/s)

The study was graciously extended the use of a *Turner Designs Model 10 Fluorometer* and supplementary apparatus by Sheffield University. In practice, the transportation of the fluorometer, tracer container, peristaltic pump and batteries was too unwieldy for one person, so it was decided instead, to manufacture a Mariotte vessel (see Plate 1) to deliver dye at a constant escape velocity to the watercourse without the need for a power source or pump, and return to the laboratory with collected samples for determination of concentration by fluorimeter.

Mariotte vessel

The Mariotte vessel was constructed in the university's public health engineering laboratory (see Plate 3.4), with a capacity of 20 litres. Calibration in the laboratory demonstrated that the device was capable of discharging at a constant rate for over an hour, meeting the requirements of the study.

Plate 3.4: Mariotte vessel.

The Mariotte vessel was employed for the first time on the 13th May 2002. Although problems were experienced with the rate of discharge (too rapid), results following measurement of the collected samples and subsequent calibration of the fluorometer were encouraging nonetheless. A plateau of discharge was attained for three sampling intervals in succession, and following calculations, discharge was found to be within 0.02 l/s of that determined by the STARFLOW. Nine further calibrations were carried out between May 2002 and January 2003 and a stage-discharge relationship calculated (figure 3.3).

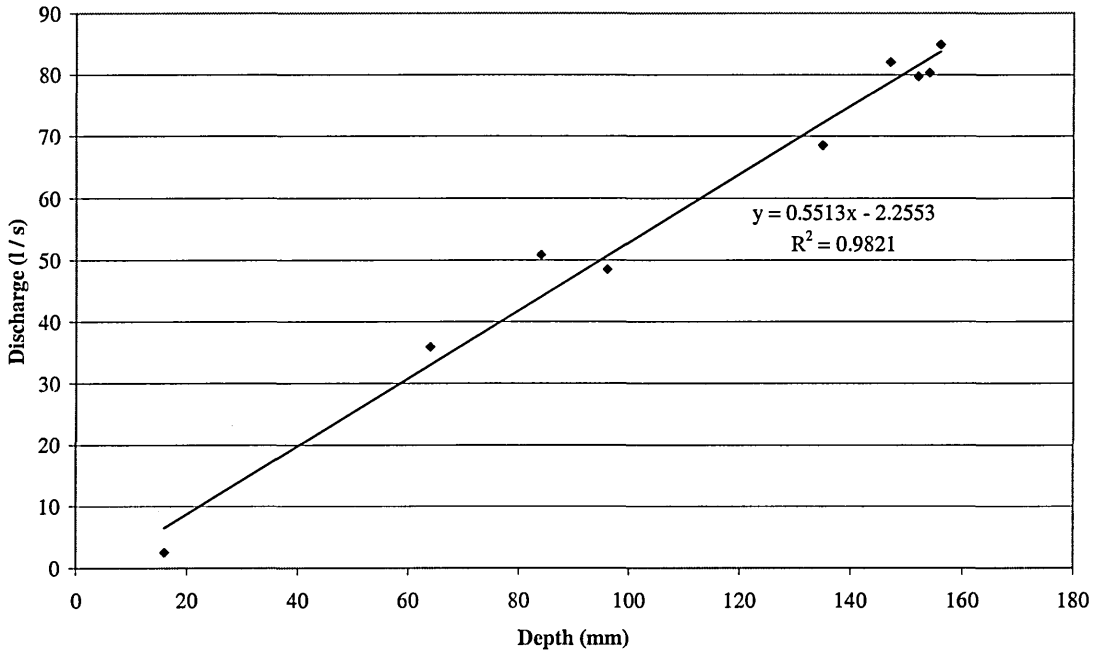


Figure 3.3: Graph of fluorimeter derived stage-discharge relationship.

3.5.2 Raingauges

Two Casella 10000E tipping-bucket raingauges and a 'Snowdon' type 8 " daily gauge were employed for the study. One tipping-bucket raingauge (rg 1) was sited with permission of Yorkshire Water Services Ltd at their Potter Hill water tower site within the study catchment (Figure 3.4). Measurement by theodolite of all structures surrounding the site confirmed that the location comfortably conformed to the Meteorological Office guidelines for the siting of rain gauges Met Office (2001). The site is sheltered on three sides and most sheltered to the west [the wind in the UK comes mainly from the west] by the water tower itself.

The second raingauge (rg 2) was emplaced on the roof of Lound Infant School within the urban portion of the catchment, with permission of the Headmistress. The school was the only structure within the urban portion of the catchment that offers a flat roof free from interference from other structures and vegetation. Advice from the Met Office (2001) contra-indicates siting raingauges above the ground; specifically on roofs and walls. Although topographically, the school roof was level with the adjacent ground (being sited within a cutting), advice from the Met Office (Hood, personal communication) was to site the gauge in a less built up area and surrounded by a turf

wall. Unfortunately, no other site existed within the urban portion of the catchment for the siting of a tipping bucket at ground level, free from the risk of interference or rain shadow.

3.6 Sampling locations

Sites for biological and biochemical sampling were located at points within the upstream rural, downstream rural, upstream urban and downstream urban portions of the catchment (Figure 3.4). A list of grid references is included below in Table 3.1.

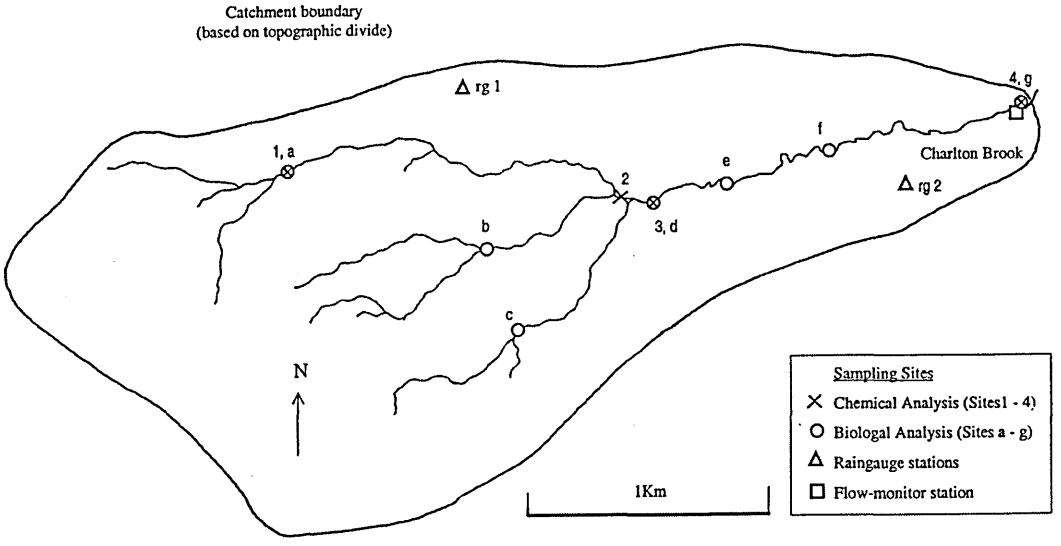


Figure 3.4: Biological and physico-chemical sampling points, Charlton brook.

Site	National Grid Reference
a (1)	SK 3255, 9672
b	SK 3355, 9645
c	SK 3363, 9613
2	SK 3391, 9656
d (3)	SK 3396, 9657
e	SK 3420, 9664
f	SK 3454, 9674
g (4)	SK 3528, 9688

Table 3.1: National Grid References for sites shown in Figure 3.3.

3.7 Summary

The background study showed that Charlton Brook was eminently suited to the requirements of the project. Blackburn Brook into which it feeds, has for many years been severely degraded, with a typical discrepancy between its biological and chemical classifications. Based on the biological assessment of the Blackburn Brook and its tributaries by Longstone (1992), the poor river quality was attributed to potentially contaminated sediments, CSO discharges, previous trade effluents, culverting and dredging (Cessford, 1997). The report concluded that there was little benefit in further biological assessment of the Blackburn Brook corridor until potential problems had been identified and remedial action taken. Charlton Brook is free from the CSOs, open cast coal sites, industrial plants and trade effluents which are a feature of the Blackburn Brook. In the context of impacts associated with urbanisation, the study site represents the opposite end of the spectrum.

Chapter 4

Preliminary study & results

4.1 Introduction

The preliminary fieldwork strategy commenced on the 7th of February 2002, with sampling of general biochemical parameters - dissolved oxygen, biochemical oxygen demand, ammonia, temperature, pH and suspended solids. Samples were obtained on a fortnightly basis from four stretches of the watercourse as indicated on the map (Figure 3.4). In addition, samples were taken from points above and below the brooks' entry to Blackburn Brook. Although not by design, subsequent interrogation of the flow monitoring data confirmed that sampling during this period in line with GQA parameters, mimicked the Environment Agency experience of typically sampling during low flows. There were two exceptions on the 14th November, 2002 and the 19th December, 2002. On the first occasion, 10.2 mm of rain fell over the catchment between 00:53 and 07:21 prior to sampling being carried out between 10 am and 12 pm. Sampling was carried out on the recessional limb of the storm in elevated flow ($\approx$ 470 mm). River flow was also elevated on the 19th December with a depth of approximately 250 mm. STARFLOW analysis showed that as before, sampling was carried out on the recessional limb of a storm. Unfortunately, due to vandalism of the school rain gauge, data for this period was not available. In any case, the results were included in the overall analysis of global water quality, as per Environment Agency protocols (E.A., 2003).

4.2 Sample collection procedures

Water samples

Midstream water samples were taken by hand, facing upstream and avoiding the disturbance of sediment. Where this was not possible, time was allowed for the sediment to disperse before taking the sample. Samples were taken in sequence from downstream to upstream, to avoid contaminating subsequent samples. All samples were collected in labelled, 2-litre polypropylene containers. Bottles were rinsed twice with sample water prior to collection of the sample. Samples were returned to the laboratory for immediate analysis. Samples for BOD determination were incubated within six hours of collection. All other laboratory determinations were carried out on the day of collection.

Storm water collection generally followed the same method employed for the regular sampling. However, all samples were taken from the same midstream point at Site G, typically at fifteen-minute intervals.

Benthic macroinvertebrate samples

At each site, samples were taken from areas of riffles within the watercourse using the standard 3-minute kick sample and I-minute manual search technique (Mason, 1996; Environment Agency, 2001), using a standard pond net (a frame of 230 mm by 250 mm, with a 900 μm mesh net of depth 275 mm, on a 1.5 m handle). The manual search involved the examination of boulders and cobbles in order to remove by hand, those organisms strongly attached and less likely to be captured during kick sampling. All organisms collected were stored in labelled, wide-necked plastic containers with a small amount of river water. After each site was sampled, the net was cleaned to ensure no organisms were still attached and therefore likely to be carried over to the next sampling point. Samples were taken in sequence from downstream to upstream to avoid impacting on subsequent macroinvertebrate assemblages. At each site, standard biomonitoring work sheets were completed, typical of those used by the Environment Agency (see Appendix II). The following characteristics of each site were noted:

- The average channel depth and sampling depth.
- The width of the channel at the point of sampling.
- The average velocity of the channel.
- Dissolved oxygen levels, temperature, pH and conductivity.
- The type and extent of terrestrial vegetation surrounding the watercourse.
- Detritus within the watercourse and the type of substrate.

4.3 Field measurements

Hand-held meters were used to measure pH, dissolved oxygen and temperature in the field on each occasion that water samples were taken for laboratory analysis. The dissolved oxygen probe was a SCHOTT Handylab OX 1/SET. The probe was calibrated on-site at measuring temperature to increase accuracy at the same frequency as the

sampling regime, using the water saturated air method as per the manufacturer's recommendations. pH was determined on site using a Schott Handylab pH 11.

4.4 Laboratory analysis procedures

Ammonia

Ammonia concentration was determined using a Hanna Instruments Colorimeter; model HI 93700, for measuring within the range of 0 - 3.0 mg l^{-1}, and a Hanna Instruments Colorimeter, model HI 93715 for measuring within the range of 0 - 9.0 mg l^{-1}. Tests for ammonia were run in triplicate with the mean of the results taken. Ammonia calibration followed the Standing Committee of Analysts (1981), recommendations using standard stock solutions of 1 mg / ml and 10 g / ml to prepare ammonia concentrations of 0.1, 1.0, 5.0 and 10 mg / l. Readings in excess of the meters range were diluted accordingly and the samples re-run.

BOD

BOD samples for General Quality Assessment determination were all undiluted with the addition of 2.0 mg ATU / L in the incubated solution. Typically, the results for the upper reaches of the brook were lower than the minimum reporting level of 2 mg / l. Consequently as per SCA (1988) recommendations, triplicate determinations were made with any outlying result discarded and the mean of the other two results quoted. Testing of storm water samples followed the same recommendations with appropriate dilution being carried out prior to incubation. Dilution water was prepared in accordance with the recommendations. The laboratory incubator was calibrated to the specified temperature of 20 ^{0}C ± 0.5 ^{0}C (SCA, 1988), by filling glass bottles with water and placing one in each corner of each shelf and checking the temperature every 24 hours, by thermometer. The thermostat was adjusted until the required temperature was achieved for all bottles at which point the thermostat temperature was noted. Thereafter, temperature was monitored continuously using a thermometer placed in a water-filled BOD bottle placed centrally within the incubator, with adjustments to the thermostat made as required.

COD

Samples were tested in triplicate for chemical oxygen demand using the micro digestion sealed tube method, in accordance with the Standing Committee of Analysts recommendations (1986). Calibration of the heating block was carried out using a wide range thermometer (0 - 300^{0}C), placed in a glycerine filled digestion tube. This allowed adjustments to be made if required throughout the digestion process.

pH

pH samples were repeat tested in the laboratory using a Hanna HI 931402 bench meter. Both the hand held and laboratory meters were calibrated using Merck CertiPUR buffers of pH 4, 7 & 10. As per the recommendations of the SCA (1988), samples were returned to the laboratory with pH measured once they were in equilibrium with the ambient temperature. Very slight error may have been introduced from using polyethylene collection containers as these may be permeable to carbon dioxide.

Suspended sediment

Suspended sediment determination followed recommendations by the SCA (1980). Samples were filtered through Whatman 70 mm glass fibre filters with a water suction vacuum pump. Triplicate samples were oven dried and weighed using an Oertling electronic balance 0.40.

Macroinvertebrates

In the laboratory, the macroinvertebrates from each site were preserved using ethanol (70% solution) to prevent decomposition as due to time constraints, identification could not be guaranteed within the proceeding 24 hours. The samples from each site were sorted in the laboratory. Each sample container was emptied into plastic trays where organic detritus and stones were rinsed and removed. The macroinvertebrates were then removed from the tray using tweezers and pipettes and

stored in petri dishes. All individuals were identified to family level with the aid of stereoscope and standard faunal identification keys (Croft, 1986; Fitter & Manuel, 1995; Hynes, 1967; Macan, 1959; Mellanby, 1965; Quigly, 1977). All families observed and their relative abundance, were recorded on standard Environment Agency forms (see Appendix II). Samples of taxa and individuals that proved difficult to identify by the author were sent to a freshwater biologist (Ms L. Beech at Wessex Water) for confirmation and identification.

4.5 Results

General Quality Assessment Parameters

Results for the period February to October 2002 were calculated following the method employed by the Environment Agency (2001). For DO, percentiles are calculated assuming a normal distribution. Given the mean, m, and the standard deviation, s, the estimate of the 10-percentile (q) is:

$$q = m - 1.2816\ s$$

The BOD and ammonia percentiles are calculated assuming a log-normal distribution. The values of m and s are thus converted to the values for the logarithms of the data (M and S respectively) using the method of moments thus;

$$S = \sqrt{[\ln (1 + s^2 / m^2)]}$$

$$M = \ln [m / \sqrt{(1 + s^2 / m^2)}]$$

M and S are estimates of the mean and standard deviation of the logarithms of the data. ln denotes the natural logarithm. The estimate of the 90-percentile (Q) is calculated using:

$$Q = e^{(M + 1.2816\ S)}$$

Where e is the constant, such that ln e = 1 (NRA, 1994). The calculated percentiles are then compared with the standards shown in table 4.3.

Parameter	Result	Site 1	Site 2	Site 3	Site 4
BOD	Mean	1.41	1.39	1.91	2.94
	SD	0.62	0.41	0.70	0.99
	90 percentile	2.21	1.93	2.82	4.24
	Grade	**A**	**A**	**B**	**C**
DO	Mean	96.79	89.68	95.22	88.99
	SD	4.92	1.25	7.27	8.43
	10 percentile	90.48	88.08	85.90	78.19
	Grade	**A**	**A**	**A**	**B**
Ammonia	Mean	0.21	0.10	0.15	0.215
	SD	0.22	0.03	0.12	0.15
	90 percentile	0.52	0.13	0.29	0.39
	Grade	**B**	**A**	**B**	**B**

Table 4.1: Chemical GQA parameters for the period February to October 2002: Charlton Brook

One-way ANOVA's were used to test whether chemical parameters differed between sites. Tukeys Pairwise Comparison was then used to determine between which sites differences occurred. There were significant differences in DO values between site 1 and site 4, ($P < 0.05$). Significant differences in BOD ($P < 0.01$) were also apparent between sites 1 and 4. Derived GQA grades also confirmed the general decline in water quality, with BOD dropping two grades and DO dropping one grade. The grade for ammonia increased from B (good) to A (very good) at site D, but subsequently declined to grade B at the lower two sites. Overall, Charlton Brook, if classified at this point, would have been graded C (fairly Good), it being the lowest grade achieved by any of the measured determinants and given that spatially, all sites are within the putative 6 km stretch of watercourse. An explanation of GQA grade assignation is given in Appendix III. Measurements taken from the Blackburn Brook told a different story (see table 4.2). The site upstream of Charlton Brook's entry to the watercourse clearly fell into the grade E classification on the strength of the high BOD and Ammonia levels. Water quality did appear to improve by the time it reached the next sampling location, some 500 metres downstream, rising two grades in the process.

Parameter	Result	Site 5	Site 6
BOD	Mean	5.971	2.764
	SD	3.291	0.803
	90 percentile	8.861	3.82
	Grade	Poor	Good
DO	Mean	89.94	87.53
	SD	14.02	8.63
	10 percentile	71.97	76.47
	Grade	Good	Good
Ammonia	Mean	0.215	0.5610
	SD	0.1460	0.3601
	90 percentile	2.83	1.00
	Grade	**D**	**C**

Table 4.2: Chemical GQA Parameters for period February to October 2002: Blackburn Brook

GQA grade	Description	Dissolved oxygen (percentage saturation) 10-percentile	Biochemical oxygen demand (mg/l) 90-percentile	Ammonia (mgN/l) 90-percentile
A	Very good	80	2.5	0.25
B	Good	70	4	0.6
C	Fairly good	60	6	1.3
D	Fair	50	8	2.5
E	Poor	20	15	9.0
F	Bad	<20	>15	>9.0

Table 4.3: General Quality Assessment (chemical grade). From Environment Agency, 2001.

This change from 'Poor' to 'Fairly Good' was felt to be due to the cleaner influent (during low flow) from Charlton Brook. There was evidence of sewage litter and 'grey water' entering the Blackburn Brook upstream of the confluence with Charlton Brook, which was particularly evident during wet weather flow (plate 4.1).

Plate 4.1: Wet weather flow at the confluence of Charlton Brook (to the left of the picture) and Blackburn Brook.

Interestingly, the Environment Agency classification of Blackburn Brook was 'Fairly Good' (Environment Agency, 2002) and was likely due to the siting of sampling stations not including the upper reaches of the watercourse.

Physico-chemical parameters

Results for the initial study are shown in tables 4.4 & 4.5 below. Applying ANOVA one way analysis of variance on the COD readings to date, showed that there was no significant difference ($p = 0.198$) between sites at the 95 % confidence interval. Similarly, neither pH nor suspended sediment showed any significant difference at the 95 % confidence interval ($p = 0.940$; $p = 0.107$, respectively). This was in contrast to the biochemical parameters which showed a significant difference for BOD ($p = 0.001$) between sites 1 & 4 and between sites 2 & 4. The COD : BOD ratio was elevated, at sites 1 to 3 possibly suggesting the presence of inorganic contaminants. The ratio of 14 : 1 at site 4 is typical of treated sewage effluent, whereby microbial treatment has

reduced the concentration of BOD in comparison to the more inert, less treatable COD. For example, according to Tebbutt (1998), substances with COD / BOD ratios of between 1 and 3 are likely to be reasonably biodegradable, but if the ratio is greater than 5, suspicions should be aroused... because high ratios can indicate the presence of dissolved organics which are largely non-biodegradable or at least only slowly broken down by biological means.

Parameter	Result	Site 1	Site 2	Site 3	Site 4
COD	Mean	33.08	38.4	50.74	41.31
	SD	28.35	36.61	37.56	36.83
	90 percentile	81.88	87.96	90.33	85.76
pH	Mean	8.05	8.0	7.96	8.04
	SD	0.34	0.39	0.35	0.23
	90 percentile	8.40	8.29	8.22	8.32
Suspended sediment	Mean	14.6	13.3	7.3	15
	SD	17.65	9.77	4.93	22.83
	90 percentile	26.72	28.32	15.2	44.76

Table 4.4: Physico-chemical parameters; Charlton Brook

Parameter	Result	Site 5	Site 6
COD	Mean	58.94	40.54
	SD	32.8	22.77
	90 percentile	82.91	72.4
pH	Mean	7.87	7.88
	SD	0.07	0.12
	90 percentile	7.94	8.02
Suspended sediment	Mean	14.9	10.0
	SD	16.9	9.51
	90 percentile	29.6	26.2

Table 4.5: Physico-chemical parameters; Blackburn Brook

Biological

Biological scores were calculated following the method employed by the Environment Agency (2003). Results from the BMWP and ASPT calculations were dramatic (see Tables 4.6 & 4.7). The upstream rural site was the most diverse, returning BMWP and ASPT scores clearly indicative of good water quality. With the onset of urbanisation, there was a marked decline in biological diversity. Between the upstream urban and downstream urban sampling sites, BMWP and ASPT declined significantly.

Definitive grading, based on the EQI calculations, illustrate a decline from A to E over the length of the watercourse. The lower than expected scores from the two ephemeral tributaries b & c, can be explained by the fact that overall macroinvertebrate assemblages from these small watercourses tend not to be characterised by high species richness (Furse, 1998) and indeed, unlikely to be colonised from adjacent streams (Griffith et al, 1998). RIVPACS software was not available, so site descriptors were given to the Environment Agency who provided RIVPACS predictions and hence, enabled derivation of EQIs. Scores were then compared to the standards for biological quality (see table 4.9).

Site	a	b	c	d	e	f	g
BMWP	147	91	95	47	32	25	19
ASPT	6.125	5.688	5.278	4.7	4.0	2.778	2.714
EQI (TAXA)	1.06	0.59	0.67	0.45	0.34	0.38	0.33
EQI (ASPT)	1.26	1.18	1.09	0.97	0.83	0.57	0.56
GRADE	**A**	**C**	**C**	**D**	**E**	**E**	**E**

Table 4.6: Macroinvertebrate data and GQA biology grades for Spring 2002.

Site	a	b	c	d	e	f	g
BMWP	123	108	80	55	42	44	24
ASPT	6.15	6.0	5.33	4.6	4.67	4.0	3.0
EQI (TAXA)	1.06	0.75	0.71	0.55	0.39	0.47	0.37
EQI (ASPT)	1.05	1.02	0.91	0.88	0.86	0.71	0.60
GRADE	**A**	**C**	**C**	**D**	**E**	**D**	**E**

Table 4.7: Macroinvertebrate data and GQA biology grades for Autumn 2002.

The two sets of macroinvertebrate data (Spring & Autumn) collected in 2002, were aggregated and scored as per the River Invertebrate Prediction and Classification System (RIVPACS) and are shown in table 4.8 below.

4.6 General trends

Overall, the observed trend is one of declining diversity and increasing abundance of inferred pollution tolerant species. This is likely due to the fact that although organic pollution generally reduces the number of macroinvertebrate species, some benefit from the increased abundance of food resulting in an increase in the total number of animals (Hynes, 1960). Site *a*, the reference site, had a diverse representation of the three most intolerant taxa; mayflies, stone flies and caddis flies representing clean water, especially with regard to organic waste (Welch, 1992). All sites from *b* to *f* whilst showing a decline in overall assemblage diversity were also characterised by the addition of one or more highly pollution tolerant or non-scoring taxa. Additions of the most sensitive taxa (BMWP score of 10) only occur within the 'rural' tributary sites. Sites *d* to *g* showed a marked decline in highly sensitive taxa with a commensurate increase in highly tolerant taxa. The transition from the rural portion of the catchment (*sites a, b & c*) to *site d* (the commencement of the urban area) coincided with the greatest single drop in assemblage numbers, diversity and sensitivity between consecutive sites. Analysis of the data confirmed that the biological quality of the watercourse was graded A (very good) for the three tributaries, dropping to C (fairly good) with the onset of urbanisation and dropping to E (poor) at the most downstream sampling site (Table 4.8).

Site	a	b	c	d	e	f	g
BMWP	183	118	128	79	45	53	31
ASPT	6.31	5.90	5.82	5.27	4.50	3.79	3.1
O/E BMWP	1.53	1.01	1.09	0.68	0.38	0.45	0.26
O/E ASPT	1.29	1.21	1.19	1.08	0.92	0.76	0.63
O/E Taxa	1.19	0.88	0.97	0.63	0.42	0.59	0.42
Grade	**A**	**A**	**A**	**C**	**C**	**D**	**E**

Table 4.8: Macroinvertebrate data 2002 aggregate: Charlton Brook.

The biological grades are based on the values of the EQIs set out in the table overleaf. The grade assigned to a site is whichever one is poorest, based on either EQI ASPT or EQI for the number of taxa.

Grade	EQI for ASPT	EQI for number of taxa	Environmental Quality
a	1.0	0.85	Very good
b	0.9	0.70	Good
c	0.77	0.55	Fairly good
d	0.65	0.45	Fair
e	0.50	0.30	Poor
f	--	--	Bad

Table 4.9: General Quality Assessment (biological grade). From Environment Agency, 2003.

Although application of the qualitative BMWP score confirmed the observed reduction in sensitive species downstream, it is based on implied tolerance and the assumption that sensitivity is not toxicant specific (Maltby, 2000). Evidence suggests that there is increasing tolerance to heavy metal pollution in the sequence from mayflies, to caddisflies to midges (Savage & Rabe, 1973; Winner *et al.*, 1975; Winner *et al.*, 1980; Solbé, 1977; Armitage, 1980). The trend within Charlton Brook has mirrored this trend showing mayflies (with the exception of the tolerant *Baetidae*) to diminish first, followed by caddisflies and finally midges, lending support to the possibility that this is an ecological response to heavy metals within the watercourse.

Work by Brooks *et al.* (1996) investigating the effects of toxicant pulses on *Gammarus pulex*; have shown that 'bursts' of cadmium equal in load to a constant 48-hr concentration resulted in significantly greater mortality. A problem with macroinvertebrate analysis is that although a given assemblage will reflect the pollution history of their site, they are also a symptom of the enormously complex mixture of pollutant inputs and processes. Although populations can recover given adequate time in clean water, the behaviour of the study catchment suggests that these periods are very rare. A study by Edwards *et al.* (1991), demonstrated that in relation to an induced pulse of reduced oxygen concentration (1mg l^{-1} for 6 hr); species recovery took between 6 to 12 weeks to return to pre-treatment abundance. Many studies suggest that toxicity resulting from stressor mixtures cannot be accurately predicted based simply on

additivity or chemical type. Indeed, some studies have shown that the interactions of chemical mixtures can change from antagonistic to synergistic based on the life stages of the organisms, concentrations of contaminants or length of exposure. The typically complex nature of pollutant mixtures however, also highlights the weakness of investigations on the impact of individual toxicants to organisms in trying to predict the impact in 'natural systems'.

Coarse particulate organic matter (CPOM) is clearly abundant within the watercourse and conforms to the generally inverse relationship between stocks of CPOM and stream order (Giller & Malmqvist, 1998). Fine particulate organic matter (FPOM) is primarily generated from the breakdown of CPOM by the activity of shredders, microbial processes and physical abrasion. In its suspended form, FPOM provides food for filter feeders such as net-spinning caddis (*Hydropsychidae*) and as a benthal / sediment source, provides for collectors / gatherers, like mayflies, cased caddis, chironomids and oligochaetes (ibid.). Dissolved oxygen is not indicated from the regular sampling strategy and indeed, experimental evidence indicates that no critical level of DO exists for macroinvertebrates in streams. Values of pH within the watercourse are typically in the range of 7 to 8 and there is some evidence that toxicity of ammonia whilst generally decreasing with increasing pH, increases again in the region pH 8 - 9 (Tomasso *et al.*, 1980; Thurston *et al.*, 1981). However, water quality standards that presently exist for fish allegedly afford more than adequate protection to macroinvertebrates as they are equally if not more tolerant to ammonia than fish (Milne *et al.*, 1992).

4.7 Summary

Results from the 2002 macroinvertebrate data presented an obvious decline in biological quality with a somewhat less clear trend in chemical quality. An unexpected mismatch was shown to exist between biology and chemistry. The upstream reference site scored more highly in terms of biology than chemistry as a consequence of ammonia levels, whereas typically, one would have expected the opposite. Over the length of the urban portion of the watercourse, results appeared to conform to expectations with biological and chemical grades becoming increasingly divergent from those upstream. However, determination of chemical grade requires 36 samples to equate to Environment Agency protocols, so in that respect, results were formative

rather than conclusive. Benthic macroinvertebrates require two samples a year from the Spring and Autumn seasons, so provided a more reliable definition of grade for 2002. Although early results suggested that the chemical decline was not as great as the biology suggested, there were signs that non-organic pollutants and / or organic pollutants more resistant to biodegradation were present within the watercourse.

Chapter 5

Survey results

5.1 Introduction

Chapter five details the results of the completed bio-chemical and biological assessments. Section 5.2 presents the results of the overall chemical grading of the study watercourse. Section 5.3 presents the data from the instream determination of heavy metals in conjunction with the Cumulative Criterion Unit (CCU) first referred to in chapter two. Section 5.4 presents the results of the biological sampling and the employment of additional ecological indices, whilst section 5.5 summarises the observations of the 2003 survey. Tables of all results can be found Appendix V.

5.2 Final chemical GQA

The regular sampling of Charlton Brook was completed (in terms of the 36 samples required as per the Environment Agencies classification procedure), in November 2003. The results are presented in the table below.

Parameter	Result	Site 1	Site 2	Site 3	Site 4
BOD	Mean	1.326	1.560	2.245	2.915
	SD	0.679	0.830	0.937	1.350
	90 percentile	2.19	2.84	3.46	5.07
	Grade	**A**	**B**	**B**	**C**
DO	Mean	94.014	92.827	91.062	83.257
	SD	6.788	7.157	8.11	14.683
	10 percentile	85.32	83.66	80.67	64.44
	Grade	**A**	**A**	**A**	**C**
Ammonia	Mean	0.118	0.177	0.229	0.396
	SD	0.140	0.133	0.250	0.549
	90 percentile	0.252	0.334	0.481	0.874
	Grade	**B**	**B**	**B**	**C**

Table 5.1: Final GQA classification Charlton Brook.

The results show a clear drop in grade from B (good) at the rural reference site (1) to C (fairly good) at the downstream urban site (4). Of equal note is the grading of B to sites 1 & 2, upstream of the SWOs. This is possibly due to agricultural application of slurry within the farmed portion of the rural portion of the catchment. Typically, grading applies to a 'stretch' of river up to 6 km in length rather than an entire watercourse. Therefore the brook could justifiably be graded according to the lowest determinand; in

this case C, even though this ignores the complexity of changes at the 'sub-stretch' level. This places the brook within the 95 % of rivers classed as having good or fair quality by the Environment Agency (2002b). Taken in isolation, the assigned chemical grade would suggest that rivers of this quality are supportive of natural ecosystems including cyprinid fisheries, suitable for potable water supply after advanced treatment (Environment Agency, 2001). Mean ammonia levels exceeded the more stringent of the freshwater fish water quality guideline values, set at 0.2 mg l^{-1} for cyprinid fisheries; the level which should be achieved where possible (78/659/EEC). Calculation of the 95 percentile level for ammonia at site 4 (1.31 mg l^{-1}), showed that levels approached the imperative guideline concentration (1.5 mg l^{-1}) set for water abstraction subject to normal treatment (75/440/EEC, & amendment 79/869/EEC). Although the watercourse itself would not be subject to abstraction, a rise in demand for abstraction, may mean that nonpoint contributions could be relevant in the future.

Parameter	Result	Site 1	Site 2	Site 3	Site 4
Suspended sediment (mg / l)	Mean	10.651	12.173	9.374	6.974
	SD	13.834	8.897	9.107	7.090
	90 Percentile	17.1	25.0	16.8	12.8
COD (mg / l)	Mean	18.877	24.560	27.814	31.429
	SD	22.743	23.850	32.116	27.383
	90 Percentile	42.40	35.38	59.76	56.996
pH units	Mean	7.959	7.918	7.891	7.904
	SD	0.307	0.290	0.255	0.272
	90 Percentile	8.189	8.250	8.192	8.209

Table 5.2: COD, suspended sediment & pH study data.

Results for the suspended sediment analysis (table 5.2) did not vary significantly from those determined in the preliminary study. The full spread of results produced a levelling out of mean concentration. All results were within the levels determined by the UWWTD for treated effluent [30 mg l^{-1}], and comfortably lower than the 50 mg l^{-1} suggested as what might be termed 'normal' for upland catchments (Tebbutt, 1998). Typical guidelines in Australia for ambient urban waterway quality is set at 25 mg l^{-1} suspended solids (Breen & Lawrence, 2003), the same as that set for freshwater fish water quality standards by the EC (78/659/EEC) and for drinking water abstraction subject to simple physical treatment with disinfection (75/440/EEC). However, mean

COD levels exceeded the guideline set for water abstraction subject to intensive physical and chemical treatment with disinfection by the EC at site 4. pH ranged from a low of 7.01 to a high of 8.75, all falling within the normal freshwater range.

BOD: COD ratios

Analysis of the field samples over the course of the study, consistently produced biochemical oxygen demand readings of between 1 mg l^{-1} and 5 mg l^{-1} during dry-weather flows. However, the mean chemical oxygen demand over the same period was 25.7 mg l^{-1}. Biochemical oxygen demand is a measure of the amount of oxygen consumed by aerobic bacteria as it biodegrades organic matter in a sample (biological oxidation). Chemical oxygen demand is the oxygen equivalent of the organic sample susceptible to oxidation by a strong chemical oxidant (APHA, 1998). The value for the COD test is therefore always greater than that for the BOD test and so is not necessarily a good indicator of BOD values for the same sample. However a high ratio of COD to BOD indicates the presence of biologically toxic material. Mean concentrations from separate storm sewer runoff have been reported as falling within the range of 33 to 265 mg/l (Ellis, 1986). COD concentrations in sewage effluents vary widely, but generally fall in the range of 10 to 100 mg/l as should be the case if conforming to the EC Directive standard of 75% removal. Unlike influents to STWs, which exhibit typical COD : BOD ratios of 2 - 4.5, effluent ratios may lie between 5 and 20 (FWR, 1997). This increase is due to the residual COD present which includes the inert non-treatable fraction. This inert fraction may be due to synthetic substances as opposed to "natural" sources of COD such as fulvic and humic acids which lend themselves more readily to biodegradation and may serve as an explanation for the COD : BOD ratio of 13.2 obtained from the study of dry weather flows in the brook. The low mean levels of BOD (2.03 mg l^{-1}) compared with the mean COD of 26 mg l^{-1} may indicates the presence of toxic contaminants. According to Ellis (1986), high ratios suggest the inhibition of biological oxidation by the toxicity of particulate materials.

5.3 Instream metal concentrations

Introduction

Water samples were analysed for a suite of metals during January and June 2004 (Appendix VI). The metals determined are shown in table 5.3 below and were chosen to

correspond with those metals for which chronic concentration criteria existed, apropos the U.S. Environmental Protection Agency criteria. Individual concentrations were then utilised to derive CCU scores which are described in this section. Metal concentrations were also determined for several storm events, but for the sake of clarity, those results are contained within chapter seven. Samples of 100 ml were filtered using Whatman 0.45 μm Membra-Fil filters and acidified by the addition of 2 % nitric acid (Aristar grade). Preliminary metals analysis was carried out on storm samples using a Spectroflame Model-P™ Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES). Calibration for Ag, Al, Be, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were carried out using standards of 5, 20 and 100 ppm. Several of the metals were found to be at levels below the limit of detection using ICP-OES and were repeated under Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), using a Hewlett Packard Agilent 4500 Mass Spectrometer, with calibration standards of 0, 100, 200 and 500 ppb.

Table 5.3: Comparison of Charlton Brook background water metal concentrations with EPA aquatic life criteria & reported freshwater ranges.

EPA Water Quality Criteria applied to Charlton Brook (values in $\mu g\ l^{-1}$)					
Metal ($\mu g\ l^{-1}$)	EPA aquatic life criteria (hardness adjusted)* CMC[1]	EPA aquatic life criteria (hardness adjusted)* CCC[2]	Charlton Brook (Mean baseflow concentration) January	June	Freshwater range (Alloway & Ayres, 1997)
Ag†	5.7	--	<lod	<lod	0.001 - 3.5
Al‡[n]	750	87	7.21	76.5	--
Cd†	2.8	0.32	0.13	0.49	0.01 - 3
Cr	751	97.63	<lod	<lod	0.1 - 6
Cu†	18.5	11.94	5.7	2.0	2 - 30
Fe[n]	--	1000	33.7	294	10 - 14000
Hg†	1.4	0.77	<lod	<lod	0.0001 - 2.8
Mn[n]	--	1000	123.2	7.35	0.02 - 130
Ni†	622	69	0.6	1.9	0.02 - 27
Pb†	93	3.6	4.5	27.3	0.06 - 120
Zn†	156	157	5.2	0.97	0.2 - 100

* Source: 'The Gold Book' (Quality Criteria for Water: 1986, EPA 440/5-86-001) and subsequent amendments; National Recommended Water Quality Criteria - Correction, 1999, EPA-822-Z-99-001 & National Recommended Water Quality Criteria: 2002, EPA-822-R-02-047.

[1] CMC: Criterion Maximum Concentration.

[2] CCC: Criterion Continuous Concentration.

† Priority toxic pollutant as per EPA. As dissolved metal in the water column.

‡ Total recoverable metal at pH 6.5 - 9.

[n] Non-priority pollutant

Cumulative Criterion Unit (CCU)

The cumulative criterion unit (Clements *et al.*, 2002) is a newly defined measure of total metal concentration and toxicity and is a modification of the U.S. EPA water-quality criteria. It is calculated for any site as the ratio of the stream metal concentration to the U.S. Environmental Protection Agency criterion values for toxicity (USEPA, 1986), the ratios being summed for all metals measured (Hirst *et al.* 2002). Clearly its utility lies in expressing the additive effects of each metal relative to postulated toxic thresholds as a single variable. Water quality criteria for individual chemicals represent levels, that when exceeded, may harm aquatic organisms. Because criterion values are only available for individual chemicals, alternative models are necessary to estimate toxic effects of metal mixtures (Clements *et al.*, 2002). The EPA metal thresholds are based on toxicity tests of species from different trophic levels, including macroinvertebrates (Hirst *et al.*, 2002). The assumption of Clements *et al.*, (2002) is based on work by others such as Enserink *et al.*, (1991) that showed the additive effects of metal mixtures at chronic concentrations.

CCU scores are calculated thus:

$$CCU = \sum_{i=1}^{n} mi / ci$$

where m_i is the total recoverable metal concentration and c_i is the hardness-adjusted criterion value for the *i*th metal.

For Al, Fe and Mn the author followed the EPA chronic criterion values of 87, 1000 and 1000 $\mu g / l^{-1}$, respectively. Due to the effects of water hardness on the toxicity and bioavailability of certain heavy metals, criterion values for Ag, Cd, Cr, Cu, Pb, Ni and Zn are modified to take this into account (USEPA, 1986). Increased hardness (increasing amounts of calcium and magnesium) reduces the toxicity of heavy metals. Copper, lead, mercury and zinc for example, all tend to be less toxic in harder waters because calcium competes with metal cations for binding sites on gill surfaces (Mason, 2002). Determination of water hardness in Charlton Brook produced values within the range of 136 to 140 mg / l, placing it in the category of *slightly hard to moderately hard*, expressed as 100 - 200 mg / l $CaCO_3$ equivalent (British Water, 2003).

Metals below the level of detection are not included in the CCU. A CCU of 1.0 is deemed to represent a conservative estimate of the total metal concentration that, when exceeded, is likely to cause harm to aquatic organisms (Clements *et al.* 2000). In the absence of fundamental intermittent standards for metals or additive cocktails of metals this method has much to commend it. The EPA criterion is stated as: ...[1] aquatic organisms and their uses should not be affected unacceptably if the 4-day average concentration of [2] does not exceed [3] $\mu g / l$ more than once every 3 years on the average and if the 1-hour average concentration does not exceed [4] $\mu g / l$ more than once every three years on the average. Where:

[1] = freshwater or saltwater
[2] = name of material
[3] = Criterion Continuous Concentration
[4] = Criterion Maximum Concentration

CCU scores were calculated for background water quality samples taken in winter and summer. The method used was the same as that employed by Hirst et al (2002) based on work by Clements *et al.*, (2000) however their studies were based on one sample per site (Ormerod, personal communication) and it was felt that results would be enhanced by comparing results from different seasons. Due to an oversight, the winter samples, taken on the 15th of January corresponded to the GQA sampling sites, whereas the summer samples taken on the 24th June correspond to the biological sampling sites. Fortunately the GQA sites 1, 3 and 4, correspond to biological sites a, d & g

Results

At all sites, CCU scores greater than 1 were determined, a level at which, if exceeded, represents a conservative estimate of the total metal concentration likely to cause harm to aquatic organisms (Clements *et al.* 2000). Winter scores ranged from 1.1 to 3.6 (figure 5.1) increasing on a gradient from upstream to downstream. Interpretation of the background water quality samples indicated that cadmium, lead and copper, were the major cause of potential impairment and to a lesser extent, aluminium and manganese. One important caveat to the results is that the CCU does not include corrections for pH. Typically, an increase in toxicity would be expected with a decrease

in pH so, as pointed out elsewhere (Hirst *et al.*, 2002), refinements to the CCU scores to account for the effects on metal toxicity at varying pH would seem desirable.

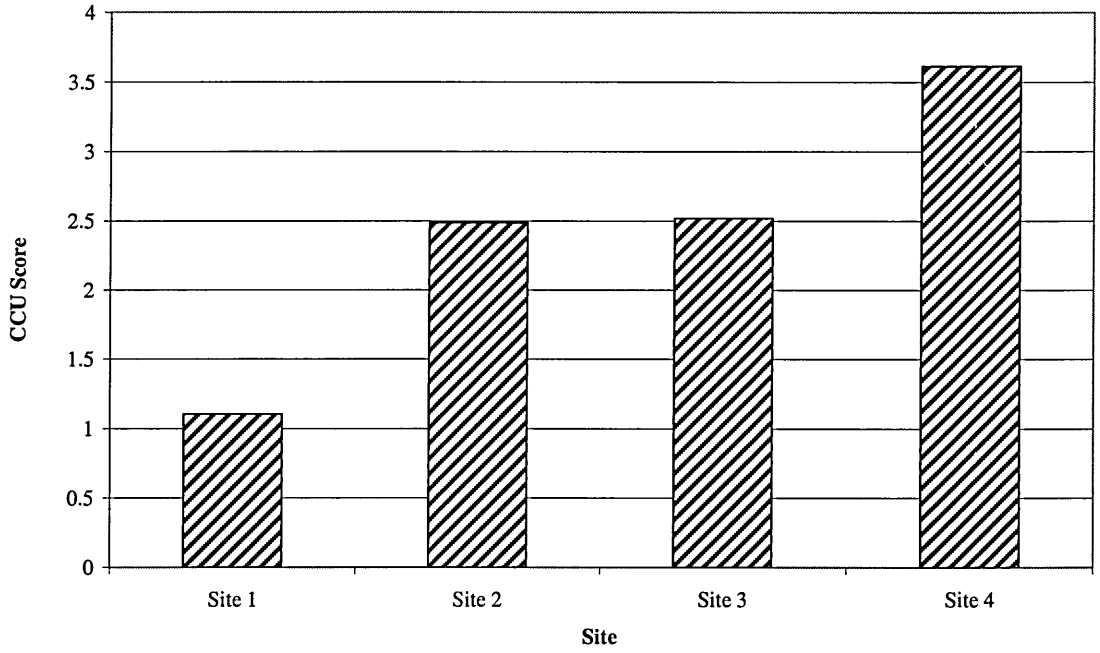


Figure 5.1: Winter CCU scores by site.

In terms of potential toxicity, lead, copper and cadmium accounted for 83 to 94 % of the contribution to overall Winter CCU scores. In terms of water-column concentration however, these three metals accounted for between 2.7 and 13.5 % of the total. Manganese was high at all sites, although in terms of potential toxicity did not exceed 25 % of the threshold level (1000 µg / l). Lead was consistently elevated at all sites, exceeding the threshold for potential toxicity within the urbanised sites, 3 & 4. Copper exceeded the threshold for potential toxicity at site 2, accounting for 43 % of the CCU score (figures 5.2 a & b). Within urban areas, copper is typically associated with vehicle brake wear, however given the rural location of site 2, possible causes of this elevation might include agricultural sources, notably fertilizers and animal waste applied to the land.

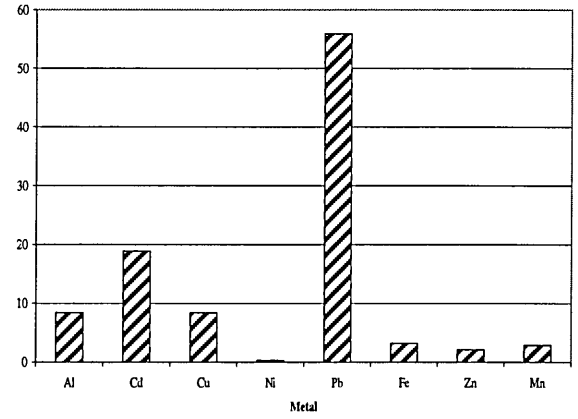
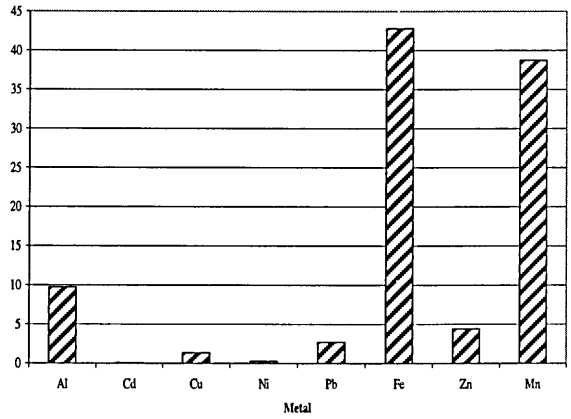
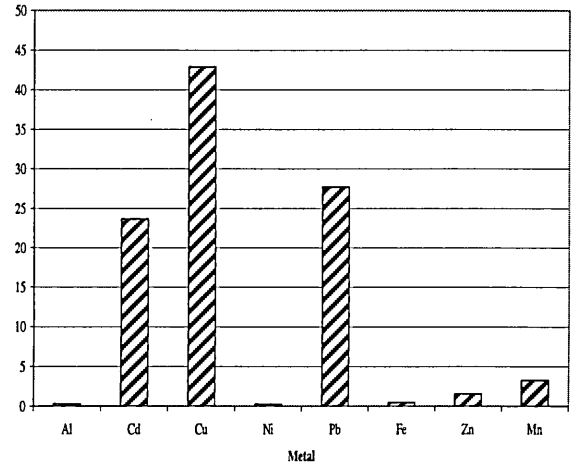
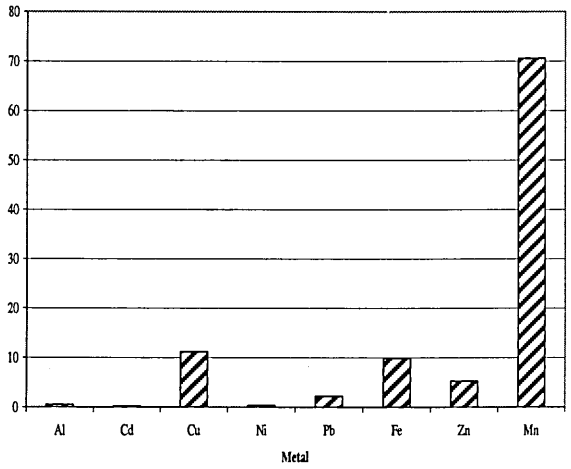
Percentage contribution of metal to derived CCU score (m_i / c_i)	Percentage contribution of metal to total instream concentration (m_i)
Site 1	
	
Site 2	
	

Figure 5.2 a: Comparison of percentage contribution to CCU score and percentage contribution of metal to total instream concentration for sites 1 & 2 (Winter).

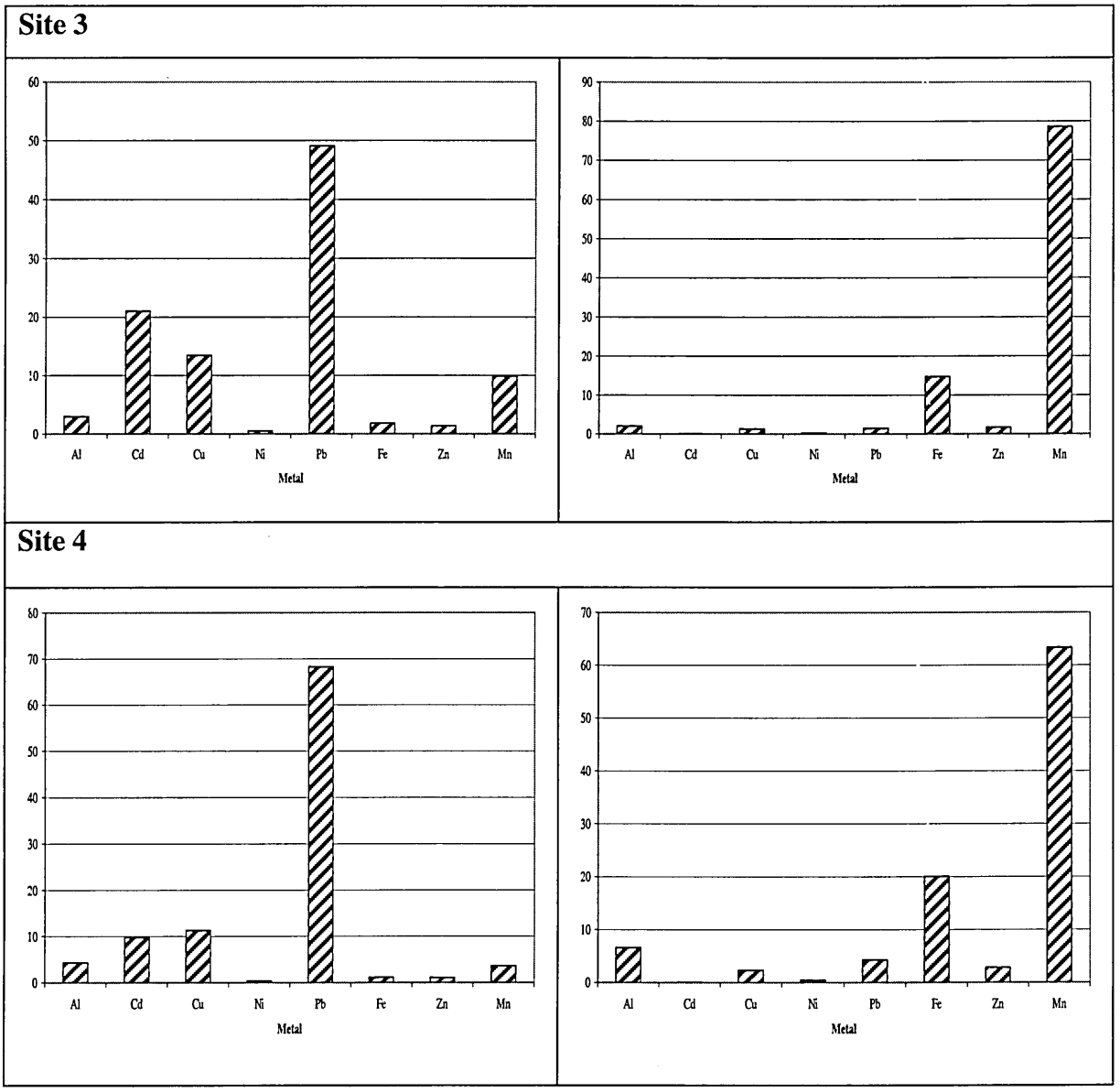


Figure 5.2 b: Comparison of percentage contribution to CCU score and percentage contribution of metal to total instream concentration for sites 3 & 4 (Winter).

The Summer scores were significantly higher for the urbanised sites, ranging from 11 to 17, although the upstream reference site remained virtually unchanged at 1.15 (figure 5.3), with lead levels an order of magnitude less than at the urbanised sites.

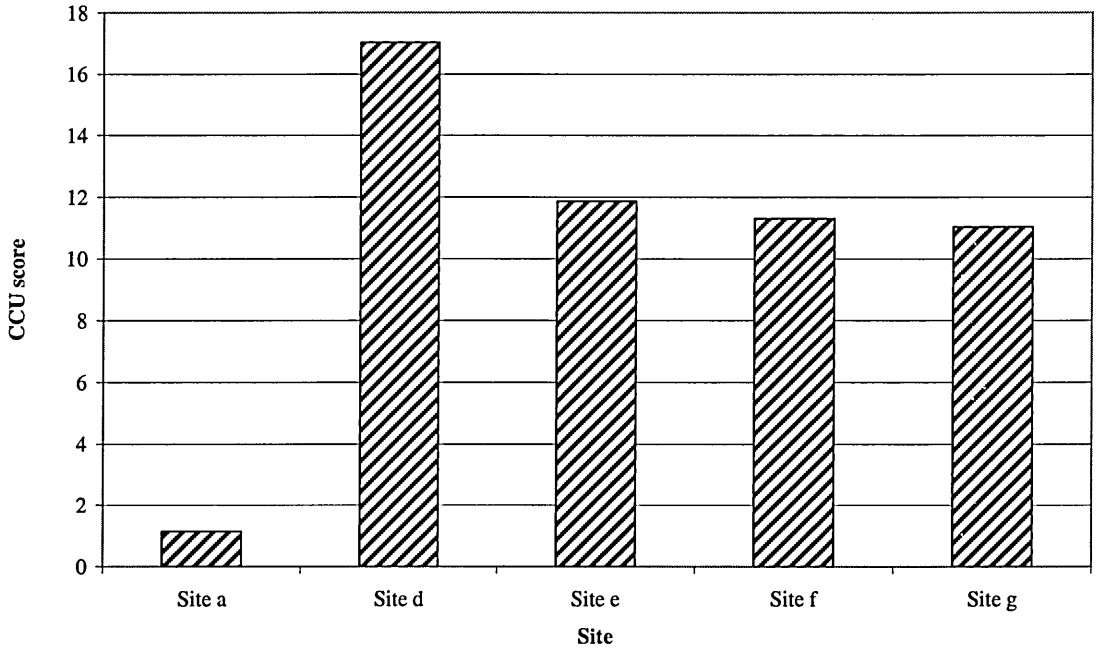
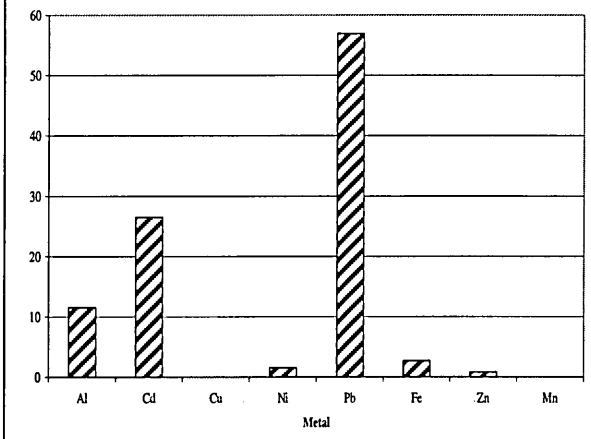
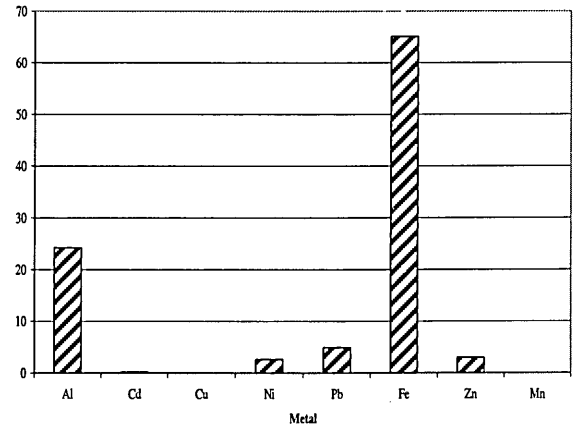
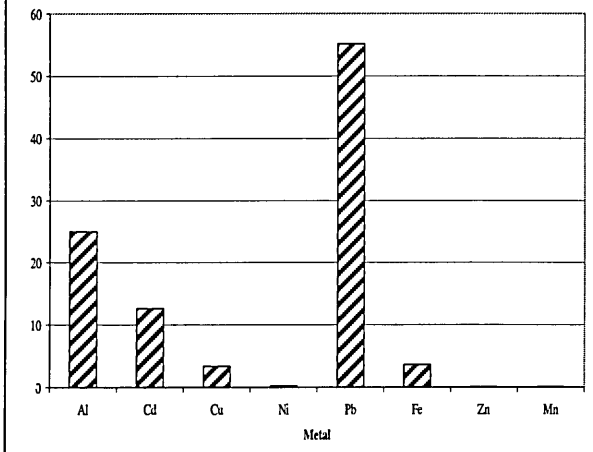
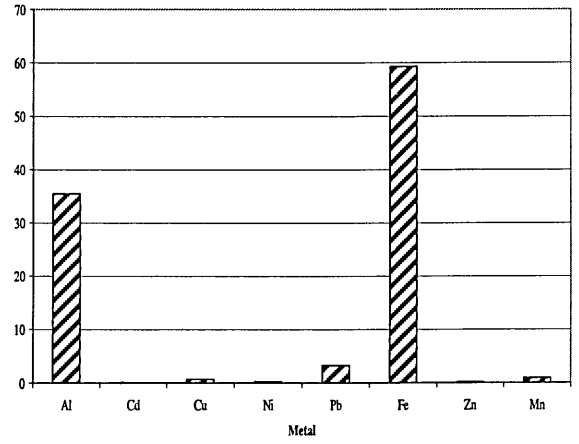
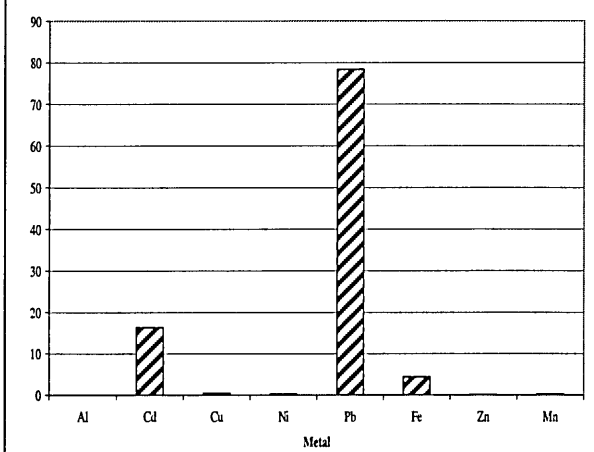
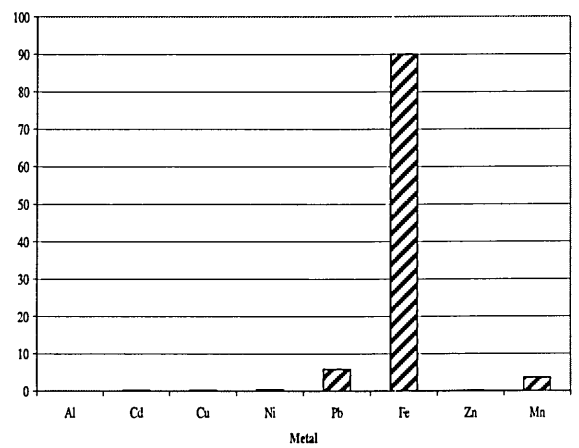


Figure 5.3: Summer CCU scores by site.

Interpretation of the Summer CCU scores (figure 5.4), showed that lead and cadmium remained major sources of potential toxicity, accounting for between 68 and 98 % of the CCU. Lead levels as a proportion of the CCU score were elevated within the urbanised portion of the catchment. The mean contribution of copper meanwhile, dropped from 19 to 1 %.

The greater levels of cadmium and lead as a percentage of criterion value (m_i / c_i) in the background samples compares with that of Clements' study, that found their importance increasing at medium-metal sites. Medium metal sites were classed as those with CCU scores between 2 and 10. Although an arbitrary distinction, these cut-off points were selected because levels at 2 - 10 times the criteria were expected to result in significant mortality of sensitive species. As toxic metals of particular environmental concern, cadmium and lead, unlike aluminium and iron, have human-induced mobilisation rates greatly exceeding that from natural sources (Novotny, cited in Salomons *et al.* 1995). The mean contribution of Al, Fe & Mn to the total instream loading remained virtually unchanged at 86 %, although this was due to a much increased contribution from iron.

Percentage contribution of metal to derived CCU score (m_i / c_i)	Percentage contribution of metal to total instream concentration (m_i)
Site a	
	
Site d	
	
Site e	
	

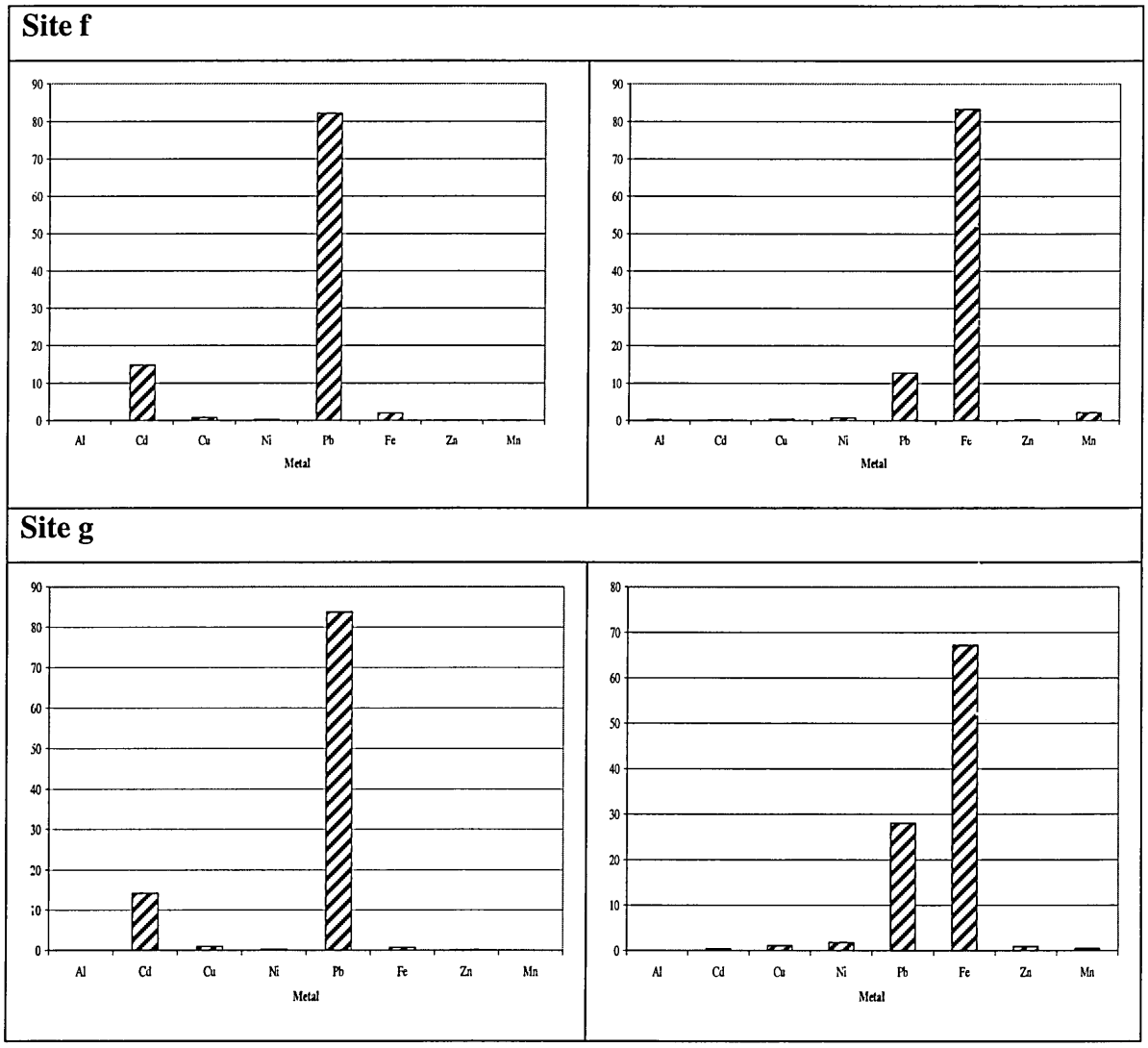


Table 5.4: Comparison of percentage contribution to CCU score and percentage contribution of metal to total instream concentration for all sites (Summer).

Summary

CCUs from the Winter sampling suggested that there was an accumulative uptake of metals as the river flowed from upstream to downstream of which the main component was lead, followed by somewhat lower levels of cadmium, copper and aluminium. Indeed, if lead is a major problem for invertebrate life in the brook, this is

cause for wider concern given that emissions of lead from petrol-engined road vehicles dropped virtually to zero in 2000 (DEFRA, 2004).

Instream concentrations showed iron increasing from 22 to 73 % of the total metal concentration with similar relative increases in aluminium and lead. Conversely, manganese declined from 63 to 1.4 % of the total instream metal.

CCU scores within the urbanised portion of the catchment were much higher in the summer, yet in both cases samples were taken during baseflow conditions. Stormwater discharges were typically reduced during the summer months, although shorter and more intense. The results therefore raise a number of possibilities. One supposition is that summer inputs of stormwater introduce greater concentrations of sediment bound pollutants, which in turn make a greater contribution to the overlying water column. Another might be that the reduced baseflows during dry periods result in reduced dilution and therefore an increased concentration of pollutants within the water column. Thirdly, increased concentration of pollutants may be as a consequence of a combination of the two.

5.4 Biology

Introduction

The following section presents the results for the macroinvertebrate sampling of Charlton Brook. The first section includes the definitive biological grading as determined in pursuance the Environment Agency protocols which utilise the BMWP scoring taxa followed by an appraisal of the individual orders of macroinvertebrates found within the brook. A list of recorded families can be found in Appendix VII.

Results

The following tables contain the macroinvertebrate data for Charlton Brook for the Spring & Autumn 2003 sampling campaigns and the aggregated data for both seasons. The striking thing to notice, is the difference between the Spring and Autumn sampling. The spring sampling highlights a grade of decline over the length of the watercourse, in comparison to the autumn where quality plummets at site d, remaining 'fair' for the length of the urbanised portion of the watercourse. Aggregated data for the two data sets as per E.A. protocols places the brook within grade D. According to the

E.A. (2003), this means that the biology is considerably different from that expected for the river in an unpolluted state.

Site	a	b	c	d	e	f	g
BMWP	134	122	128	84	79	70	27
ASPT	6.7	6.78	6.73	5.25	5.27	5.38	3.38
O/E ASPT	1.07	1.40	1.39	0.94	0.92	0.91	0.63
O/E No. Taxa	0.88	0.97	1.03	0.72	0.64	0.55	0.37
Grade	**A**	**A**	**A**	**B**	**C**	**C**	**D**

Table 5.4: Macroinvertebrate data Spring 2003: Charlton Brook.

Site	a	b	c	d	e	f	g
BMWP	133	---	---	56	48	51	40
ASPT	6.05	---	---	5.09	4.0	4.64	4.0
O/E ASPT	1.03	---	---	0.98	0.74	0.82	0.70
O/E No. Taxa	1.04	---	---	0.50	0.52	0.48	0.47
Grade	**A**	**---**	**---**	**D**	**D**	**D**	**D**

Table 5.5: Macroinvertebrate data Autumn 2003: Charlton Brook.

Site	A	B*	C*	D	E	F	G
BMWP	158	122	128	96	85	78	40
BMWP taxa	24	18	19	18	17	14	11
ASPT	6.58	6.78	6.73	5.33	5.0	5.6	3.64
O/E ASPT	1.34	1.40	1.39	1.09	1.02	1.15	0.74
O/E Taxa	0.99	0.97	1.03	0.76	0.71	0.59	0.46
Grade	**A**	**A**	**A**	**B**	**B**	**C**	**D**

Table 5.6: 2003 aggregate GQA derived grades and indice scores. * Figures for sites B & C are spring values as the two southerly tributaries had completely dried up at the time of the Autumn sampling.

The biological grades are based on the values of the EQIs set out in table 5.7 overleaf. The grade assigned to a site is whichever one is poorest, based on either EQI ASPT or EQI for the number of taxa.

Grade	EQI for ASPT	EQI for number of taxa	Environmental Quality
A	1.0	0.85	Very good
B	0.9	0.70	Good
C	0.77	0.55	Fairly good
D	0.65	0.45	Fair
E	0.50	0.30	Poor
F	--	--	Bad

Table 5.7: General Quality Assessment (biological grade). From Environment Agency, 2003.

Oligochaeta (Aquatic worms)

Oligochaetes are the lowest scoring of the BMWP taxa and are generally considered to be indicative of organic pollution, although their value as an indicator has been questioned (Walley & Hawkes, 1996; Weibel *et al.*, 1966) due to the basing of the taxa's sensitivity on known highly tolerant families such as *Tubifex tubifex* and *Limnodrilus hoffmeisteri*. Oligochaetes are common in most freshwater habitats and are the only order present at every site sampled on Charlton Brook. During the spring sampling their absolute abundance reached a peak at the most downstream site (figure 5.5) with relative abundance only being checked by the massive rise in asellidae numbers. Given the additional absence of any sensitive species at the bottom sites it is possible in this case that the taxa were a measure of organic pollution. Indeed, the aforementioned *Tubifex* and *Limnodrilus* are the only macroinvertebrates that occur downstream of gross organic pollution in high numbers (Weiderholm, 1984). Oligochaetes have also been found to be highly tolerant of metal pollution (Mason, 2002). However, during the autumn sampling, *Oligochaeta* numbers were much reduced at the downstream site, with sites *a* & *d* having the greatest percentage abundance.

Percentage abundances are calculated thus: $A = \frac{n}{N}$

where n is the number of individuals from a specific subset of a sample and N, is the total number of individuals within the sample.

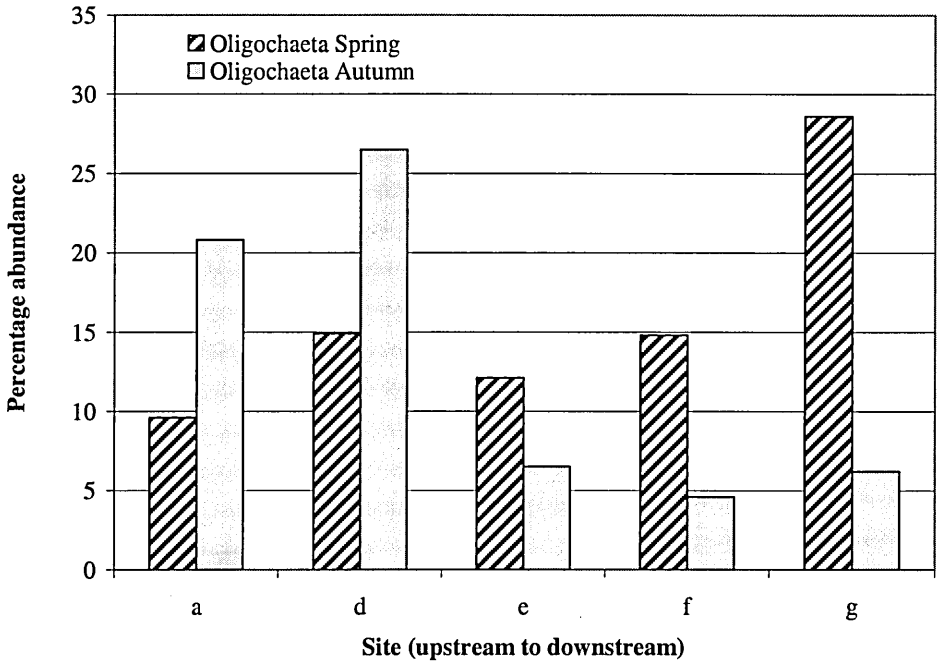


Figure 5.5: *Oligochaeta* percentage abundance within Charlton Brook.

Crustacea

Gammaridae were present at all sampling sites with the exception of site *g* in the spring. They are stressed by ammonia levels in excess of 0.2 mg/l (CIES, 2002) which partially explains their much reduced relative abundance from *site d* onwards, and it has been demonstrated by others, that a positive relationship with *gammaridae* mortality and total ammonia exists (Mullis *et al.*, 1996). Absence of *G. Pulex* may be related to stresses imposed by extreme episodic events, and/or to chronic exposure following storm disturbance of benthic sediments which have been contaminated by intermittent polluted discharges (Shutes *et al.*, 1992). Absence of *G. Pulex* in other studies (Shutes, 1984b) has also been postulated as a response to trace metals and hydrocarbons in water and bed sediments. The trend of declining *Gammaridae* abundance was very clear from the autumn sampling in comparison to the spring (figure 5.6), suggestive of changing water quality within the brook.

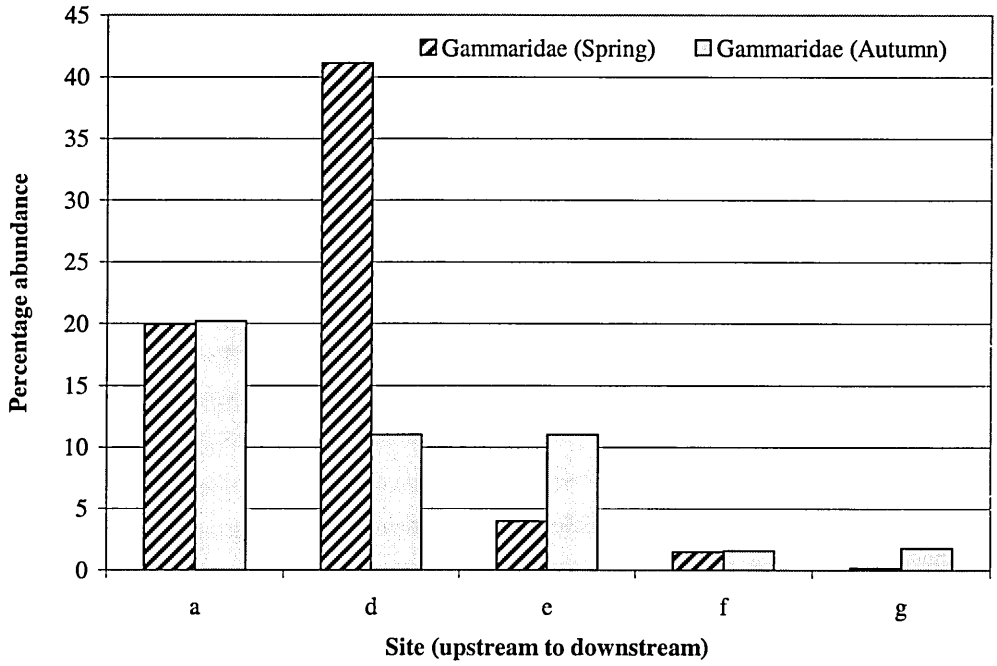


Figure 5.6: *Gammaridae* percentage abundance within Charlton Brook.

The sensitivity of *G. Pulex* to trace metals and hydrocarbons in water and bed sediments (Rehwoldt et al., 1973), may explain their dip in numbers at *site d* and their continued reduction following the onset of urbanisation. Conversely, *Asellidae* were in abundance from *site e* onwards (figure 5.7).

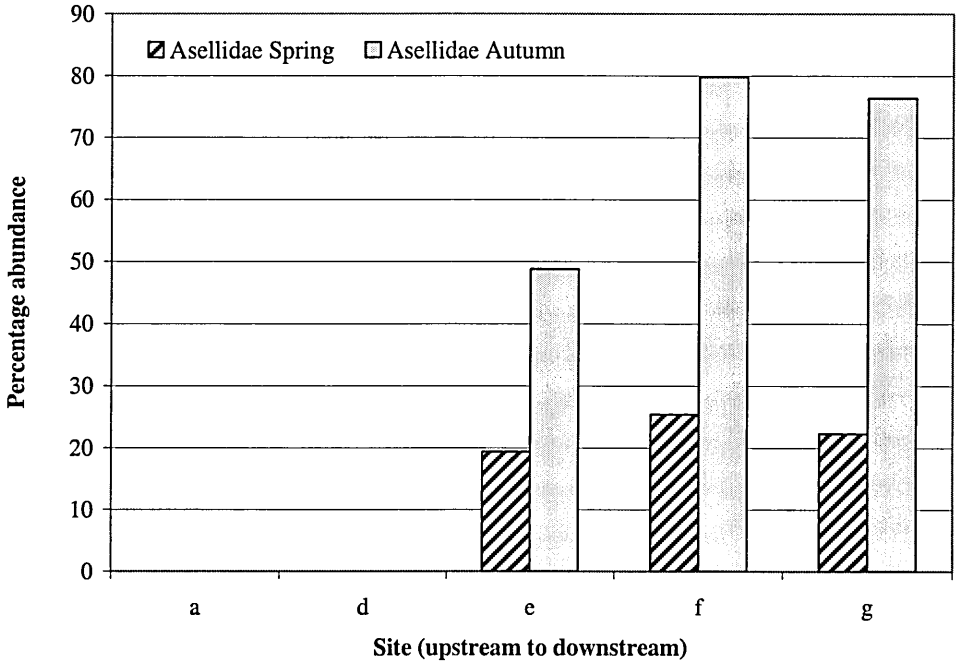


Figure 5.7: *Asellidae* percentage abundance within Charlton Brook.

Asellidae are quite tolerant of low oxygen conditions and in organically polluted streams it invades riffles (where it is not naturally found) to replace *Gammaridae* (Hawkes, 1979). The measured GQA determinants are not indicated per se, however *Asellidae* have been found to be tolerant of heavy metals (Brown, 1976; Mason, 2002) and to prefer the organic enrichment of pollution (Wright, 2002). Indeed, Mullis *et al.* (1996) surmise that *Asellidae* are less sensitive to ammonia and other pollutants typically associated with sewer effluents. Additionally, the autumn percentage of *Asellidae* at sites *e, f* and *g* (49, 80 & 76 % of the total) is a clear indicator of community instability and that a stressor is present (Plotnikoff, 1998), being found naturally at the most highly polluted river sites (Shutes *et al.*, 1992).

Hirudinea (leeches) & Tricladi (flatworms)

Two families of *Hirudinea* were present in the watercourse; *Erpobdellidae* and *Glossiphonidae* although *both* were absent from the rural catchment in Spring & Autumn. Greatest overall numbers occurred at site *e,* in tandem with the greatest rise in numbers of *Asellidae. Glossiphonidae stagnalis*, a common form of the taxa is known to feed on *Asellidae* but despite sharing the same tolerance to organic pollution, did not appear to have increased its abundance to match that of its prey at site *g*. One reason may be that it is in fact, more intolerant of pollution than the BMWP score suggests (Walley & Hawkes, 1996). The lower abundance of *Glossiphonidae* than *Erpobdellidae* may also be explained by its habitation of a typically narrower BOD_5 range (CIES, 2002). However, leeches are typically widespread and more limited by physical factors such as high levels of siltation so their presence at all but one site may not be useful as an indicator of pollution or otherwise. Indeed, they occupy an important niche in maintaining the health of all watercourses. Tricladi (*Planaridae*), were only present at sites *a* & *e.* They are prey to leeches and their greater abundance at site *e* may also help to explain the rise in leech numbers at site *e* from 37 to 132 between the spring and autumn sampling.

Coleoptera (Beetles)

Despite being the largest group of insects world-wide, Coleoptera were all but absent from the reference site and although found in relatively much greater numbers in the middle tributary, were absent from sampling sites e, f and g. The presence of *Elmidae* is typified by streams shaded by dense riparian vegetation, providing allochthonous material and the woodland habitat surrounding the middle tributary certainly conforms to this. However, riparian vegetation is abundant for the length of the watercourse and the determinants measured for the GQA were not indicated. Coleoptera are only moderately pollution sensitive, so other factors must have a bearing on their virtual absence from the watercourse.

Plecoptera (Stoneflies)

As a group, the Plecoptera contain the highest percentage of the most sensitive macroinvertebrates used in the BMWP scoring system. The upstream reference site held five families [*Chloroperlidae, Leuctridae, Nemouridae, Taeniopterygidae* and *Perlodidae*]. With the onset of urbanisation, stoneflies were all but absent from the remaining sites (figure 5.8) and remained absent over the rest of the watercourse. Plecoptera made small inroads to the urban sites in a change from 2002, with sites d, e & f, boasting small numbers during the spring sampling [7, 7 & 3, respectively]. More interesting perhaps, was the absence of stoneflies, with the exception of one *Perlodidae* at site d, by the autumn, reflecting the general trend in the reduction of biological quality over the course of the year. Empirically derived ammonia and BOD_5 values from site d onwards are indicated (even before consideration of other inputs) in the absence of all *Plecoptera* taxa. Derived values would place *Plecoptera* at or within the extreme upper limit of their range.

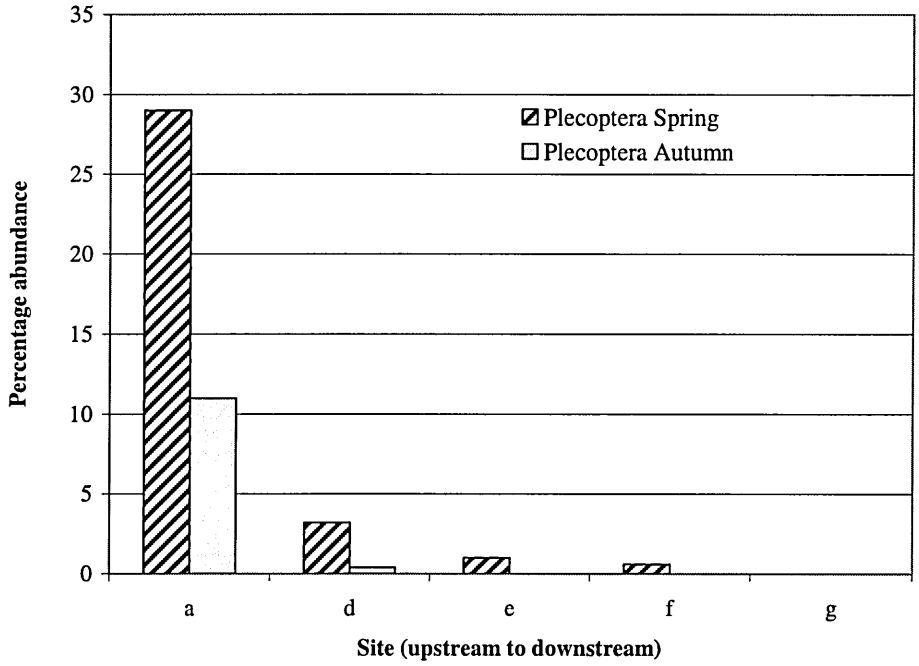


Figure 5.8: *Plecoptera* percentage abundance within Charlton Brook.

Tricoptera (Caddis Flies)

Tricoptera were present at all sites to varying degrees with the exception of *g*, which was devoid of this order in Spring and contained only one *Limnephilid* in the Autumn. This was not unexpected given the overall trend of decline in biological diversity (figure 5.9). The majority of Tricoptera used as indicator species (56%) are highly sensitive and thus high scoring, with seven families represented at the upstream site. However, overall numbers of Tricoptera were buoyed at sites *e* and *f* with the presence of lower scoring families; i.e. *Hydropsychidae, Polycentropodidae* and *Limnephilidae*, the former being suggested as able to tolerate some amount of organic pollution (Stroud Center, 2002), preferring higher nutrient waters (NAMC, 2002), as well as being the lowest scoring of the order. An increase in *Hydropsychidae* as a percentage of the total assemblage can be taken as a measure of stream impairment, when considering composition measures (U.S. EPA, 2002 (figure 5.10). The converse also holds true with the percentage *Tricoptera* decreasing downstream when *Hydropsychidae* are removed from the equation. Levels of BOD_5 and ammonia typified by the downstream end of the watercourse would be indicated in the decline and / or absence of the *Sericostomatidae*, *Rhyacophilidae* and *Hydroptilidae* families.

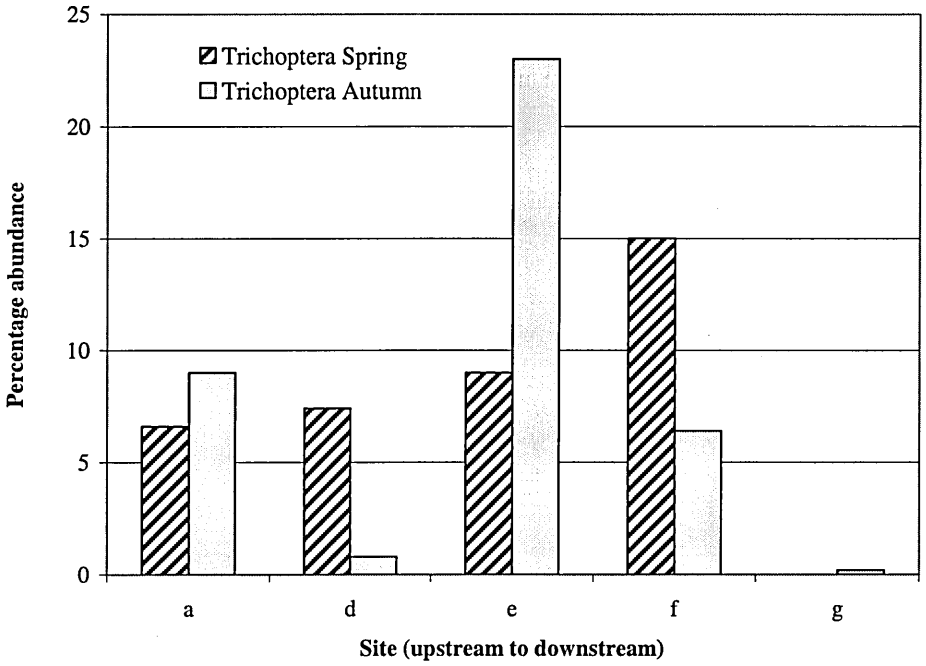


Figure 5.9: *Trichoptera* percentage abundance within Charlton Brook.

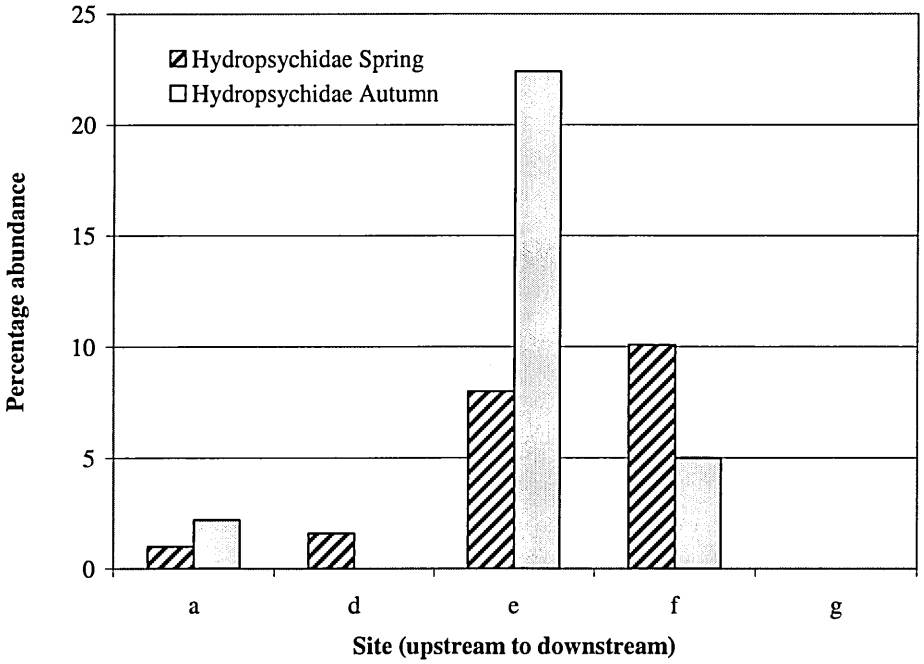


Figure 5.10: *Trichoptera & Hydropsychidae* percentage abundance within Charlton Brook.

Ephemeroptera (Mayflies)

Ephemeroptera were represented by two families on Charlton Brook; *Baetidae,* and *Heptagenidae*. The latter is highly intolerant of changes in water quality and was

only found at the reference site in significant numbers. Spring samples showed that *Baetidae,* although present at the reference site, was virtually absent from site *d*, returning in significant numbers at subsequent urban sites. By the autumn, mayflies were virtually absent from the urbanised portion of the catchment. Using composition measures, an increased percentage of *Baetidae* within the mayfly assemblage is recognised as a response to stream impairment (U.S. EPA, 2002), for example, in comparison to *Heptagenidae*, *Baetidae* are more tolerant of BOD_5 and ammonia for example. Results in this respect would probably have limited value within the study as with the exception of site a where *Baetidae* forms 50 % of the mayfly assemblage, it accounted for 100 % at all other sites (figure 5.11).

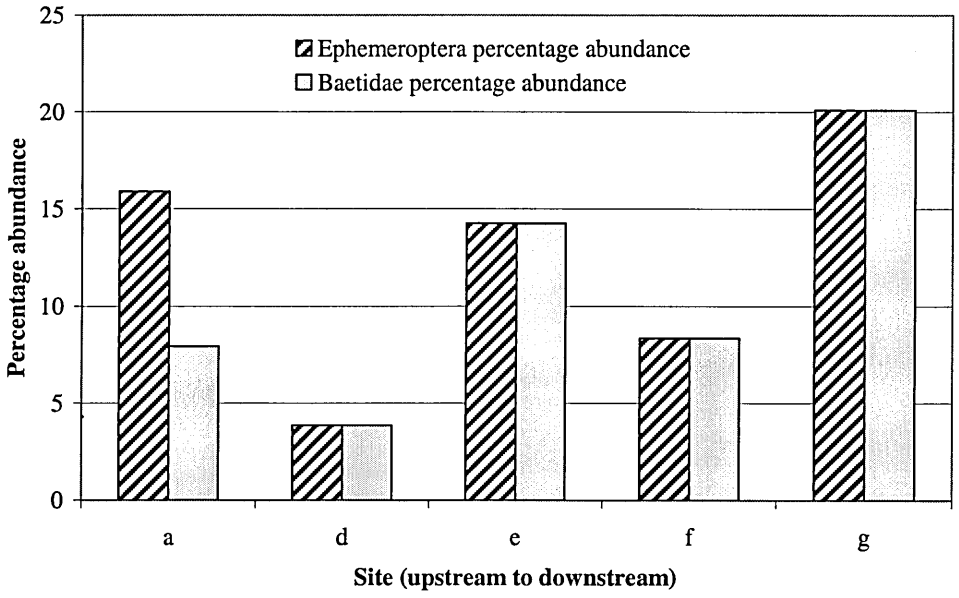


Figure 5.11: *Ephemeroptera* & *Baetidae* percentage abundance within Charlton Brook.

Diptera (True Flies)

Diptera were represented within the watercourse by the families *Tipulidae*, *Chironomidae* and *Simulidae*. The latter were only found in numbers at site *a*. During the spring sampling, *Tipulidae* were present from sites *a* to *e*, however they were all but absent from the urban sites during the autumn sampling. *Chironomidae* were most abundant at site *f* and are considered to be highly pollution tolerant. According to Welch (1992), continued increases in organic wastes will ultimately favour the decline of

Chironomidae in favour of *Oligochaeta*. The processes within the brook do not follow a trend in this respect as shown in figure 5.12.

An increased ratio of worms (*Oligochaeta*) to *Chironomidae* can indicate the presence of inorganic pollution and potentially this is supported by the increased numbers of the heavy metal tolerant *Asellidae* at the most downstream site. This is commensurate with Shutes' (1984a) statement, that Dipteran larvae are particularly sensitive to trace metals, although the family *Chironomidae* are reported as being unaffected by metals (Mason, 2002). Overall ratios of *Oligochaeta* to *Chironomidae* (figure 5.13) are inconclusive in this respect however with no obvious trend emerging. *Chironomidae* numbers reduced significantly at site *e* between spring and summer 2003 and may also be allied to the relatively high numbers of *Hirudinea* who depend on true-fly larvae as a major food source (Shutes, 1984). Diptera are also associated with nutrient enrichment (Plotnikoff, 1998). *Tipulidae* prefer an abundance of leaf litter, twigs and associated fungi (NAMC, 2002) and these are readily available at all sites, so clearly food availability is not the limiting factor at the three most downstream sites.

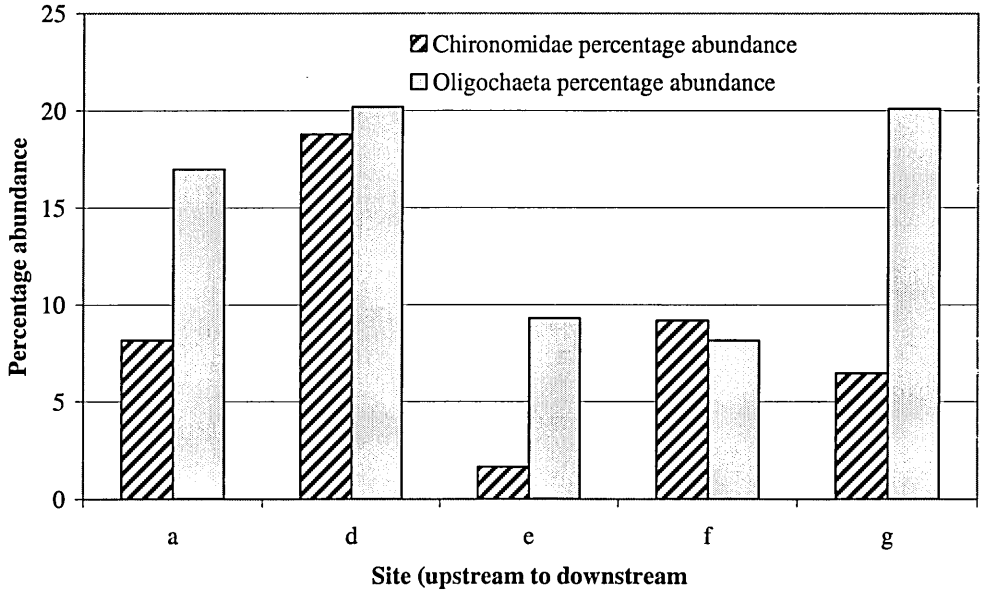


Figure 5.12: *Chironomidae* & *Oligochaeta* percentage abundance within Charlton Brook.

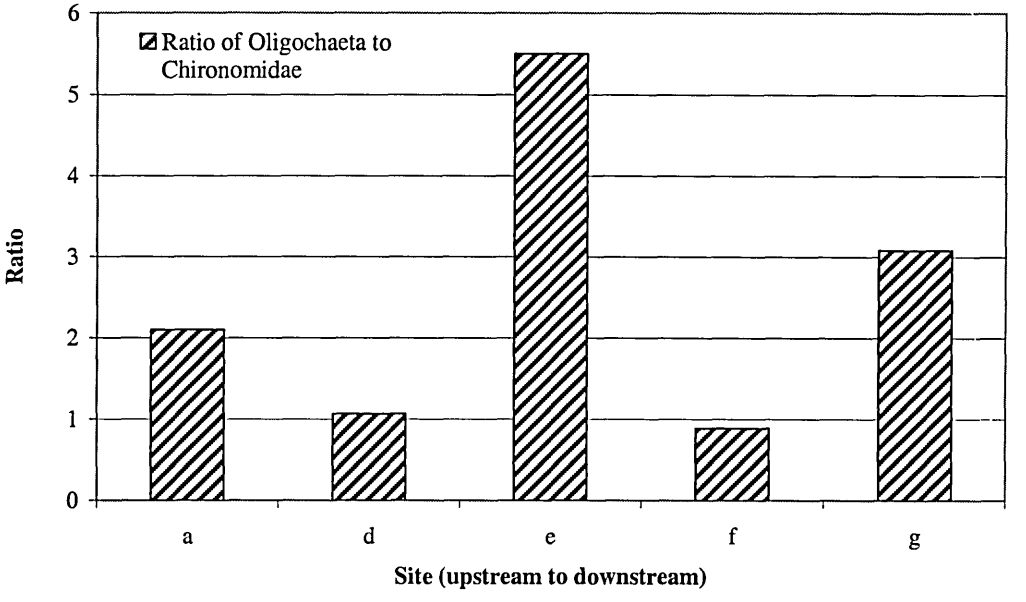


Figure 5.13: Ratio of *Oligochaeta* to *Chironomidae* within Charlton Brook.

Mollusca

The molluscs were most abundant at sites, *a* and *d*, particularly *Lymnaeidae* and *Hydrobidae*. With the exception of *Ancylidae*, the taxa collected from Charlton brook exhibited an organic pollution tolerance similar to *Asellidae*. The more sensitive *Ancylidae* was only present at site a. As fairly sedentary organisms they reflect local conditions and are effective bioaccumulators of toxicants from environmental concentrations that are near or below the limit of detection in chemical analysis (Heinonen, 2001) and are recognised as being very tolerant of low oxygen conditions. Additionally, neither pH nor hardness are implicated within the brook. The absence of mature *Sphaeridae* may be an indicator of disturbance, but the specific causes are unknown. *Hydrobidae*, an indicator of poor water quality in springs (Ragavan & Sada, 2000) was the dominant family at site *d*, accounting for 61 of the 62 molluscs present. Over the course of the summer in 2003, numbers increased significantly at sites *a* and *d*, although increased numbers were limited to single figures at the remaining sites and overall numbers were very low (figure 5.14).

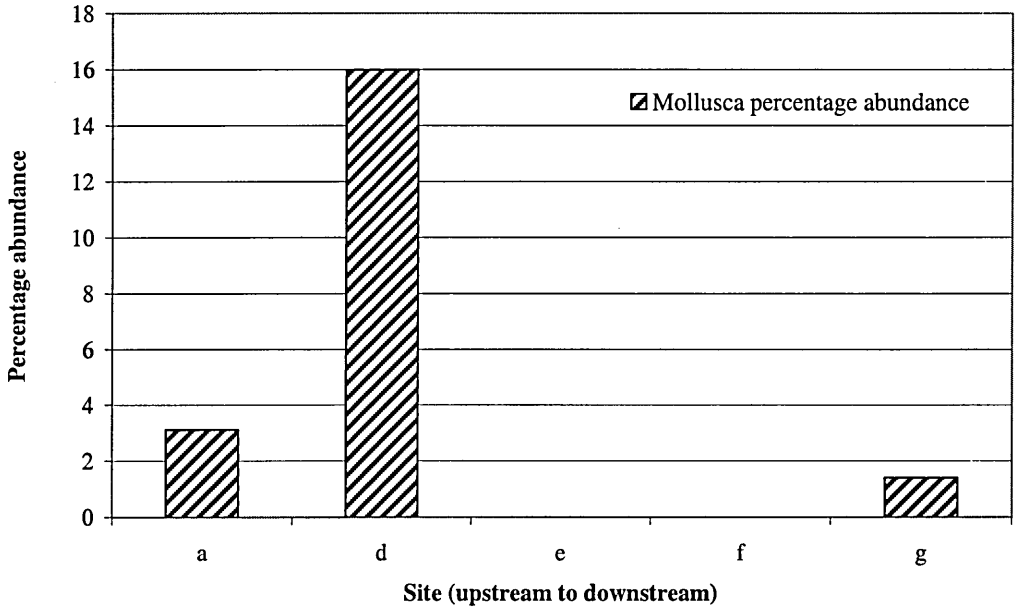


Figure 5.14: *Mollusca* percentage abundance within Charlton brook.

Summary

Overall grading of the sampling sites showed no change for the rural tributaries. However, the urban sites (*d* to *g*) all increased by one grade between 2002 and 2003. BMWP scores ranged from 40 to 56, a much reduced spread compared to the spring samples which ranged from 27 to 84.

The following graphs (figures 5.15 & 5.16) illustrate the consistent overall trend of dropping BMWP score and number of taxa with increasing urbanisation. Figure 5.17, which illustrates the pattern of ASPT along the watercourse is interesting as it again shows site *f* as being anomalous to the general trend. However, in 2003, the increase was for ASPT and not BMWP or number of taxa, reflecting the inclusion of one stonefly and two additional caddis fly families with a commensurate reduction in *Mollusca* taxa. Of the two caddis additions, one is *Sericostomatidae,* a highly sensitive taxon, which has appeared at all urban sites this year with the exception of *site g*, although its numbers could not be classed as abundant. Other trends that persisted from 2002 were the absence of *Asellidae* up to *site d* and the complete dominance of *Baetidae* among the mayfly assemblage. *Trichoptera* numbers peaked again at site e, declining to

virtually zero at site *g*. The *Hemiptera* were again absent from all sites and *Coleoptera* were, as in 2002, absent from *sites e, f* and *g*.

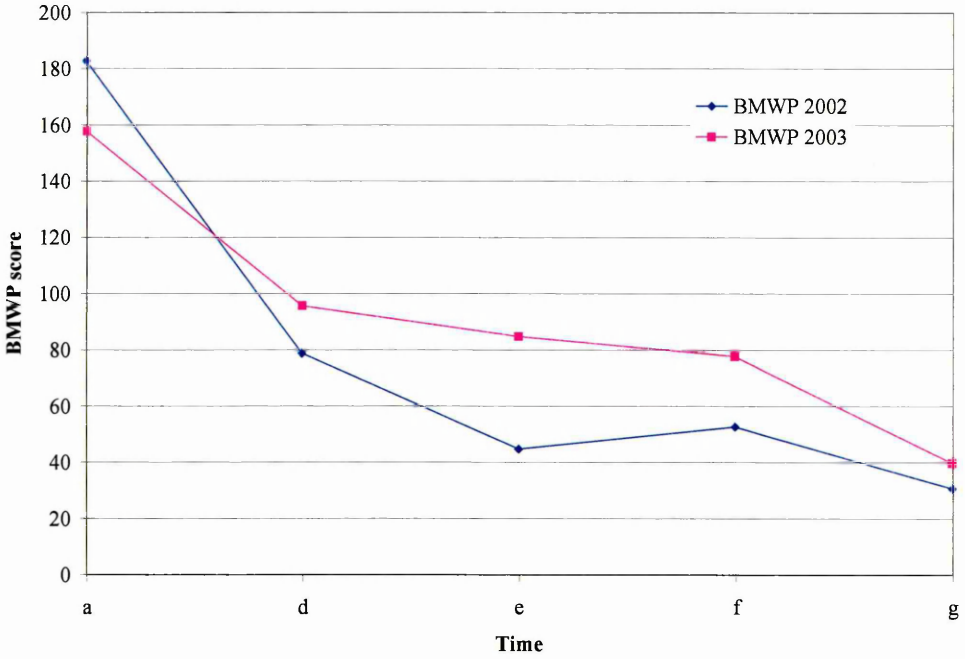


Figure 5.15: BMWP comparison for 2002 and 2003.

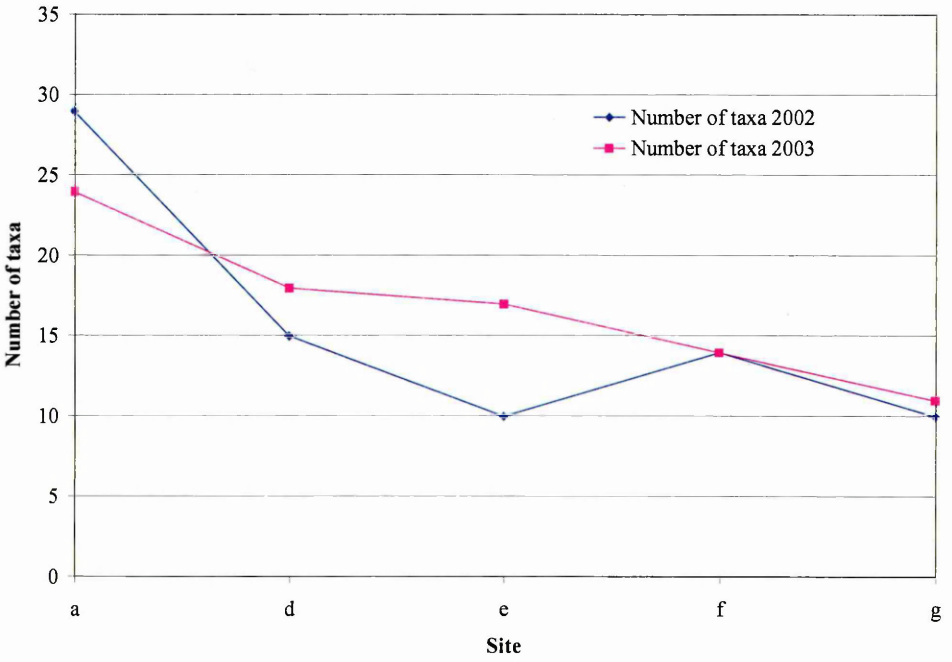


Figure 5.16: Number of taxa comparison for 2002 and 2003.

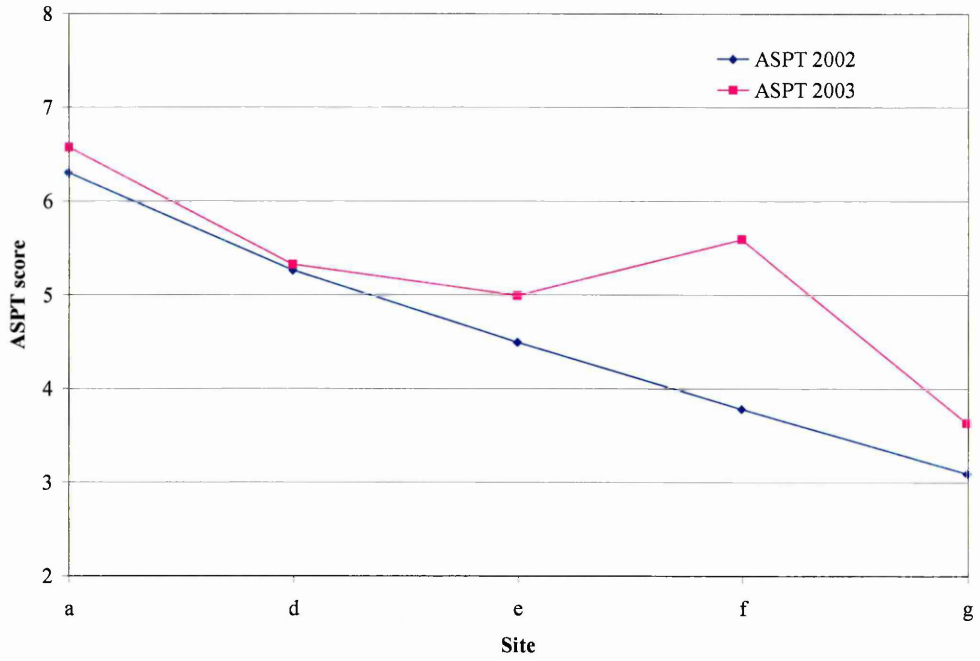


Figure 5.17: ASPT comparison for 2002 and 2003.

The 'phenomenon' of reduced macroinvertebrate assemblage below outfalls is widely documented (Mason, 2002; Coomhola Salmon Trust, 2001; Maltby *et al.*, 2000; Maltby et al., 1995; Payne & Hedges, 1990; Seager & Abrahams, 1990; Resh & Unzicker, 1975; Hynes, 1960), yet determination of the distances required for total recovery to be effected are less well determined, with recovery tending to be expressed in dimensionless terms (Mason, Streamscapes, *ibid.* Hynes, 1960). Work by Milne *et al.*, (1992), observed that there was a consistent depression in macroinvertebrate scores immediately downstream of CSOs with partial recovery towards upstream levels at sites further downstream. At 250 m downstream, community status was similar to that at upstream sites. Evidence also pointed to dry periods preceding rainfall events having an enabling effect on macroinvertebrate recolonisation. Indeed, every study site recorded an increase in the number of individuals sampled from the previous year with *site e* showing a 550% increase. The smallest increase was recorded at *site g* (13%).

Diversity indices

Species richness, or number of taxa, is the simplest measure of biodiversity within a sample. Most pollution indices such as BMWP, rely on the appearance or

disappearance of indicator species. The BMWP score is based on the allocation of a score ranging from 1 to 10 to the invertebrate families in a sample, with each family scoring once, irrespective of abundance. The ASPT, is simply the total BMWP score divided by the number of different scoring taxa, and was initially used to avoid bias from sampling effort. Calculation of ASPT, which is independent of sample size, is a quick and straightforward scoring system regarded as a stable and reliable index of organic pollution (Environment Agency, 2003). However, these indices based on sensitivity to organic pollution, were considered insufficient in ascribing the potential effect of pollution that includes contaminants more specific to stormwater such as trace metals. Diversity indices which are based on the premise that pollution causes reduced diversity and increased relative abundance are therefore, applicable to any type of pollution (Haille, 2000). Various indices of diversity, most notably Simpson's index and the Shannon-Wiener index have been devised to take into account variation in abundance distributions when making comparisons between samples (Ricklefs & Miller, 2000). These indices weight the contribution of the relative abundance of each species to the total assemblage. Consequently, diversity indices were employed in the study. Additionally, Pielou's evenness index was employed in analysis of the biological data, based on all families present within the samples.

The Shannon-Weiner index (*H'*), is the most widely used diversity index (Pires et al., 2000; Ludwig & Reynolds, 1988). It appears to be the most consistently useful way of obtaining significant diversity indices which are relatively independent of sample size (Štirn 1981) and by some (e.g. Štirn 1981; Gray *et al.* 1992, cited in Environment Canada, 2001) has been recommended the most suitable expression of biotic diversity. The Shannon-Weiner index is the measure of the uncertainty to which group a randomly selected individual will belong, with the uncertainty increasing as the number of species increases. A greater number of species increases species diversity, as does a more even or equitable distribution among the species. In theory, the higher the value of *H'*, the greater the diversity and supposedly, the healthier the environment. An obvious weakness of the index, is that irrespective of the environment from which the sample was taken, a few, evenly distributed families could still result in a high value of *H'*. For example, 14 evenly distributed species of chironomid worm would produce an *H'* of 2.64, which compares favourably to site *a* on Charlton Brook with an aggregate *H'* of 2.63. Therefore, careful observation of the species patterns is required in order to interpret the values effectively. Despite this problem, the utilisation of diversity indices

can aid in data reduction and in combination with the other indicators of community structure such as richness, evenness and abundance, allows the interpretation of environmental condition and the visible effects on macroinvertebrate organisms (Pires *et al.*, 2000). Values of the index for real [sic] communities typically fall between 1.5 and 3.5 (Ohio University, 2002).

Shannon-Weiner index: $$H' = - \sum_{i=1}^{s} (P_i \ln p_i)$$ (Ludwig & Reynolds, 1988)

where, H' is the index of species diversity, s = the number of different species, $p_i = n_i / N$ where n_i is the number of individuals within species i, and N is the total number of individuals of all species.

Simpson's (dominance) index, a similarly useful tool to aquatic ecologists, is the measure of the probability that two randomly selected individuals from a sample belong to the same species or family. It is represented by the formula:

Simpson's index: $$D = \sum_{i=1}^{s} p_i^2$$ (Ludwig & Reynolds, 1988)

where, p_i is the proportion of the ith species, given by $p_i = n_i / N$. D is influenced by two parameters - the equitability of the percentage of each species present and richness. For a given species richness, D will decrease as the percent of the species becomes more equitable. Simpson's index D, gives the probability that two randomly selected individuals will belong to the same family. Simply stated, if the probability is high that both individuals belong to the same species, then the diversity of the community sample is low (Ludwig & Reynolds, 1988). The reciprocal of D conversely, gives the probability that two randomly selected individuals will belong to different species A commonly used alternative expression of the index is $1 / D$ (d), to provide a comparative measure of diversity (Ricklefs & Miller, 1999; Ohio University, 2002). This overcomes the somewhat confusing situation whereby a value approaching 1, represents an increasingly less diverse assemblage. The Simpson index gives less weight to rare species than to common ones, belonging to the category of dominance indices that attach more importance to abundant species (Mouillot & Leprêtre, 1999).

As diversity indices alone do not specifically indicate the degree to which species within a sample are evenly abundant, evenness measures are typically employed, in this case, Pielou's evenness *J'*, illustrated by the formula:

Pielou's evenness: $$J' = \frac{H'}{\ln(s)}$$ (Ludwig & Reynolds, 1988)

where, *H'* is the Shannon-Weiner index, ln is the log base (e), and *s* is the number of taxa. The index expresses *H'* relative to the maximum value that *H'* can obtain when all of the species in the sample are equally abundant with one individual per species. Values range from 0 to 1.0 with increasing evenness as the score approaches 1. Pielou's *J* is affected by species richness, which is unsurprising, given its relationship to *H'*, which assigns greater weight to rare species

Results

The total assemblages at each site were mathematically transformed in order to calculate the indices described above. Tables 5.8 & 5.9 show the resultant indice scores for the macroinvertebrate samples

Site	**a**	**d**	**e**	**f**	**g**
Families	22	19	16	12	8
Shannon-Weiner (*H'*)	2.49	2.0	1.90	1.91	1.54
Simpson's (*D'*)	0.11	0.21	0.22	0.18	0.25
Simpson's *d* (1 / *D'*)	9.35	4.73	4.56	5.62	4.06
Pielou's evenness (*J'*)	0.79	0.68	0.69	0.77	0.74

Table 5.8: Diversity scores: Spring 2003.

Site	**a**	**d**	**e**	**f**	**g**
Families	27	12	14	14	13
Shannon-Weiner (*H'*)	2.51	1.63	1.53	0.90	0.66
Simpson's (*D'*)	0.12	0.23	0.31	0.64	0.59
Simpson's *d* (1 / *D'*)	8.31	4.32	3.24	1.55	1.68
Pielou's evenness (*J'*)	0.76	0.65	0.58	0.34	0.26

Table 5.9: Diversity scores: Autumn 2003.

The most obvious trend is that associated with the simplest measure of diversity; taxa richness, with the numbers of different macroinvertebrate families declining by 70 % over the length of the watercourse in the spring. Simpson's index indicates that site A was the least likely to be dominated by one species (Figure 5.18), although as the evenness measures show, all sites despite their differing number of taxa were similarly even in their distribution (Figure 5.19). Overall diversity (*H'*), as a combination of richness and evenness shows a clear trend of decline over the length of the watercourse.

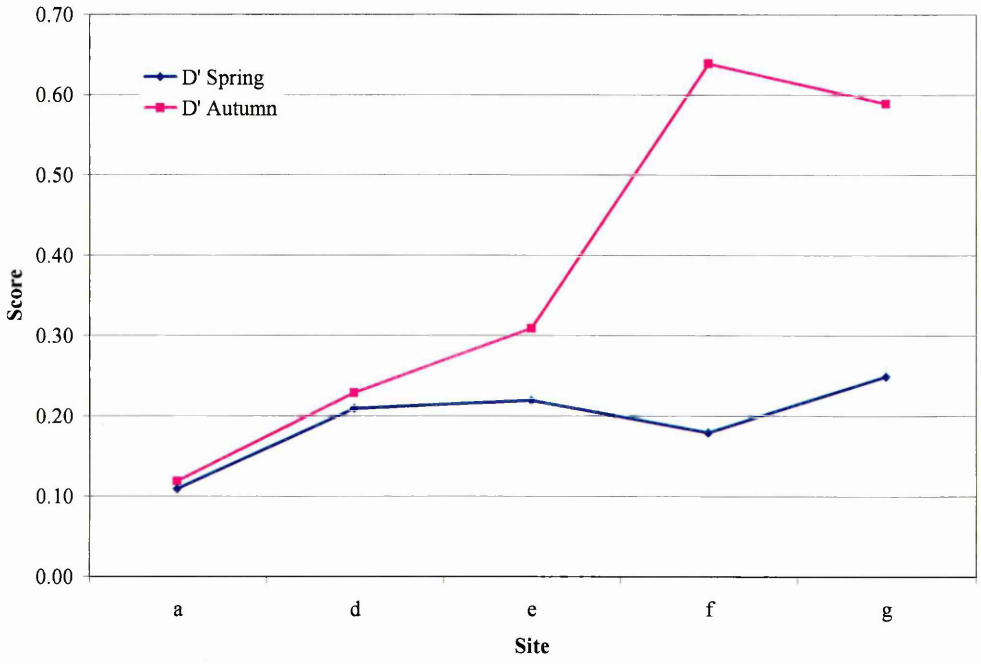


Figure 5.18: Comparison of Spring & Summer scores for Simpson's *D'*

The autumn scores highlight an exacerbation of the decline noted in the spring. Simpson's index scores show that for the bottom three sites, there was an increasing dominance of a few pollution tolerant taxa, notably *Asellidae*, which increased in number six-fold at site F, comprising 80 % of the assemblage.

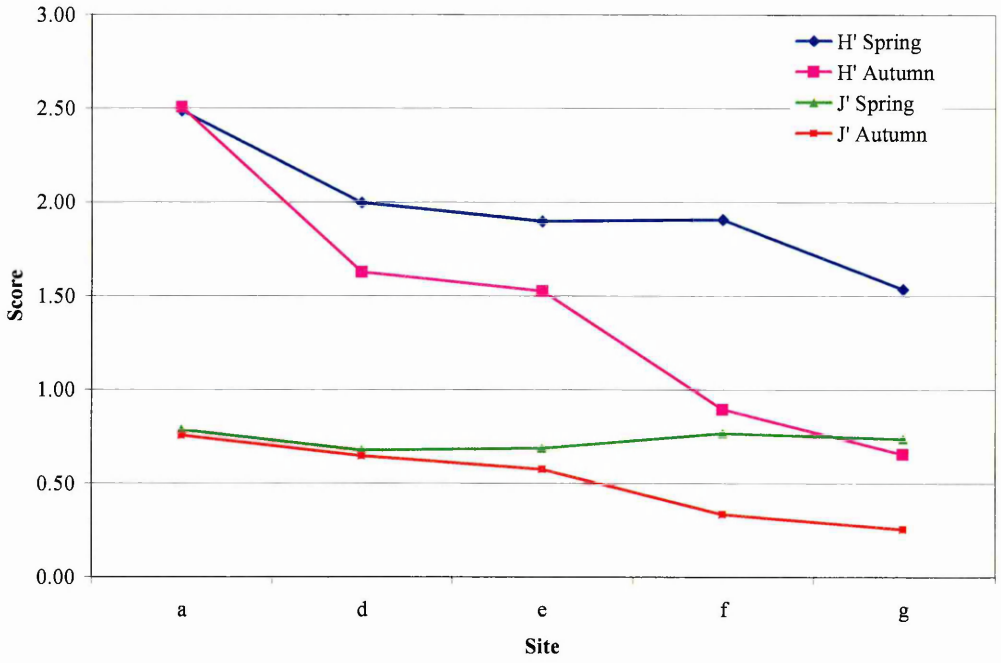


Figure 5.19: Comparison of Spring & Summer scores for Pielou's *J'* & Shannon-Weiner's *H'*.

The apparently greater diversity at site *g* than at site *f* can similarly be explained its slightly reduced dominance of *Asellidae* at the site The Shannon-Weiner scores correlated significantly with BMWP in Spring ($P = 0.001$) and to a lesser degree in the Autumn ($P = 0.050$). This is not surprising given that all the spring samples were dominated by BMWP taxa. Autumn samples in comparison, contained a higher number of non-BMWP scoring taxa. The importance of sensitive families to the biodiversity of the brook and their self evidently smaller total numbers, would suggest that the Shannon-Weiner and Pielou indices were appropriate in interpreting the streams' diversity. The Simpson's scores meanwhile, served to confirm the effect of dominance by a smaller number of families at certain sites.

5.5 Summary

During the course of the study, data was collected for two spring and autumn sampling campaigns. Analysis of the data showed that site *d* had the highest proportion of chironomids at any of the sampling stations, often seen as a general indicator of pollution (Winner *et al.*, 1990). Comparing data for other indicator species at the site confirmed this, notably due to the presence of the amphipod *Asellus aquaticus*. Over the

two year sampling period, the overall percentage of *Gammaridae* declined from 27 to 10 % of the total assemblage (Spring 2002 to autumn 2003). Comparing spring and autumn data for 2003, confirms that the trend is one of decline over the summer period. *Gammaridae* as a percentage of the total declined in 2003 from 38 to 10 %. Over the same period, the percentage EPT taxa declined from 18 to 2 %. The percentage EPT for 2002 in comparison, declined from 22 to 16 % of total assemblage. Site *g*, the least diverse of the sampled sites demonstrated a similar trend in water quality decline with *Asellidae* increasing from 22 to 76 % of the total assemblage. Results from 2002 also confirm this seasonal decline, albeit less severe, with *Asellidae* increasing from 35 to 60% of total assemblage at site *g*. (Figure 5.20). Reasons for the exacerbation of this trend in 2003 are not fully understood, although it seems reasonable to suppose that the untypically dry weather experienced in 2003 may be responsible. Seager & Abrahams (1990) for example, noted that differences in biotic scores between upstream and downstream sites were reduced during periods of no rainfall. This was clearly the case within the urbanised part of the watercourse. However, potential improvements within parts of the brook, by the addition of taxa, were seemingly nullified by the proliferation of single dominant families.

Despite the apparent richness at the reference site for both seasons, there were changes within the assemblage with a decline in EPT from 64 to 27 %, and an increase in *Mollusca*, *Diptera*, *Hemiptera* and *Hirudinea*. Stoneflies are moderately tolerant of low levels of trace elements and are commonly one of the earlier groups to recover after influxes of trace elements (Clements, 1995, cited in Mize & Deacon, 2002). This may explain the occurrence of very small numbers of *Leuctridae*, *Perlodidae* and *Taeniopterygidae* at some of the urban sites. However, the abundance of *Plecoptera* showed a distinct decline over the length of the river. *Chloroperlidae*, indicated as sensitive to moderate zinc concentrations (Mize & Deacon, 2002) were completely absent from the urban sites.

Evidence suggests that there is increasing tolerance to heavy metal pollution in the sequence from mayflies, to caddisflies to midges (Savage & Rabe, 1973; Winner *et al.*, 1980). Site *e* however, had the highest proportion of mayfly and caddis fly in the spring, suggesting that it was the least polluted site in terms of metals (Winner *et al.*, 1990). Simple manipulation of the data by removing *Baetidae* and *Hydropsychidae*; suggested metal tolerant species (U.S. Fish & Wildlife Service, 2004, Mize & Deacon, 2002), from the scores, highlights a different trend (Figure 5.21). The site was heavily

buoyed by *Hydropsychidae,* which comprise 96 % of the total EPT assemblage. Heptagenid mayflies which are considered less tolerant to trace element contamination (Clements & Kiffney, 1994; Mize & Deacon, 2002) were all but absent from the urban sites and *Ephemeroptera*, significantly declined at all sites between the sampling campaigns, most noticeably within the urbanised sites. Overall, the site with the lowest assemblage of caddis and mayflies was *g* , the most downstream site. Possibly this is an indication that the combination of pollutant inputs to the river are at their most synergistic at this point. Increasing perturbation is also suggested by declining *Diptera* numbers (Barbour *et al.*, 1996), a feature of the changing assemblage at sites *e*, *f* and *g*, over the course of the year.

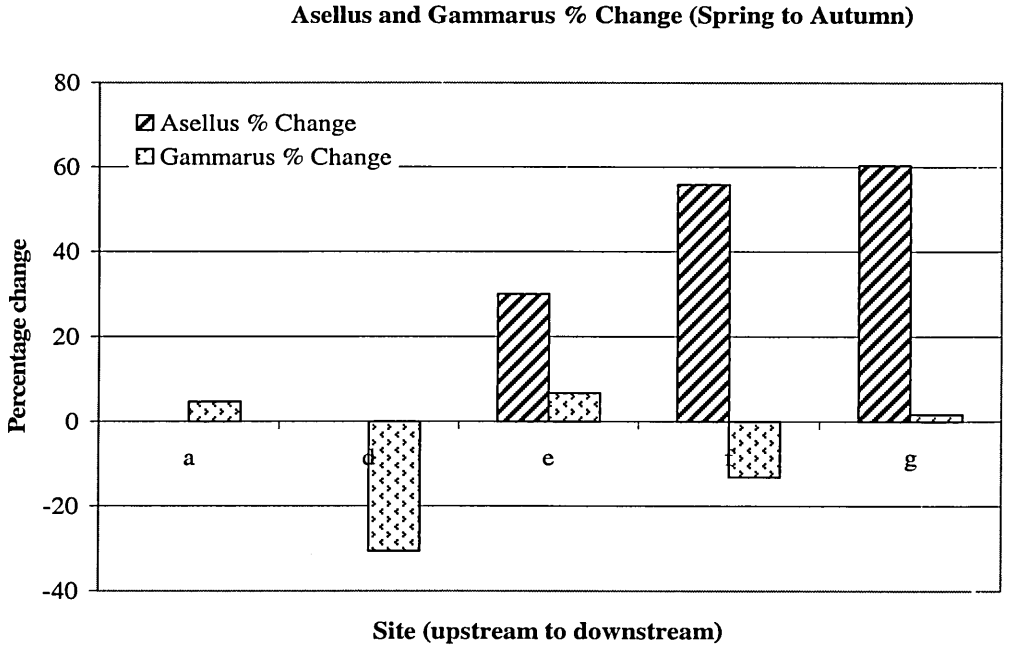


Figure 5.20: Comparison of percentage change in *Gammaridae* and *Asellidae* abundance 2003.

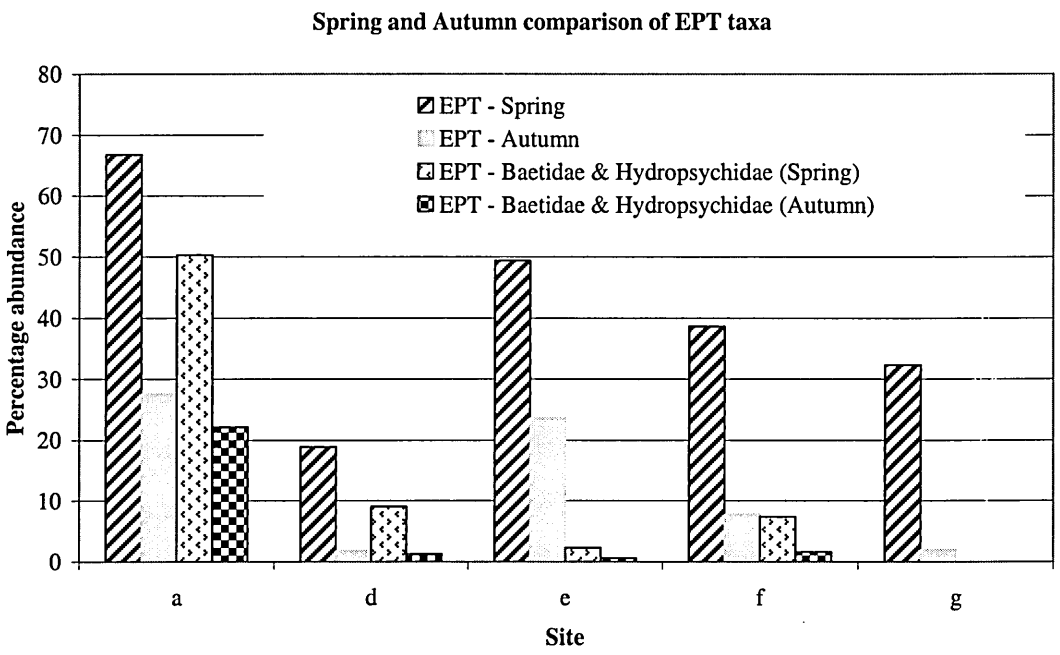


Figure 5.21: Comparison of EPT assemblage, Spring & Autumn, 2003.

Dry weather resulted in the two lower tributaries completely drying up in the period between the two sampling campaigns. This is not an unusual phenomenon for small headwaters, particularly for southern chalk streams and is reported elsewhere in the literature (Pires *et al.*, 2000; Lake, 2003; Wright *et al.*, 1994). According to Lake (2003), understanding of the effects of drought on the ecology of flowing waters is limited. The consequences of this in terms of recolonisation are also unclear but evidence suggests that losses of abundant species may cause major changes in community structure and a marked lag in recovery (Boulton & Lake, 1992; Boulton *et al.*, 1992; Resh, 1992, cited in Lake, 2003). This would go some way in determining whether the comparatively depauperate assemblage in the lower tributaries is a consequence of seasonal drought within sections of the stream and responsible for reduced EPT assemblage within the upper tributary.

Chapter 6

Investigation of sediment pollutants

6.1 Introduction

Chapter six deals with the analysis and interpretation of the sediment-bound pollutants determined during the study. The background to their inclusion is discussed followed by sections on the collection and preparation of the samples. Determined concentrations are then presented in comparison to standards. Section 6.8 summarises the observations of the sediment investigation.

6.2 Background

From the 2002 analysis of the macroinvertebrate assemblages within the Brook, it was apparent that the decline in diversity may not have been simply a response to organic pollution. Sediments are indicated as the cause of beneficial use impairments (Burton & Pitt, 2001) with some going so far as to state that the accumulation of contaminated streambed sediments is the principle underlying reason for reduced biointegrity (Beasley & Kneale, 2002). Similarly, Burton *et al.* (2000) state that contaminated sediments tend to be the greatest threat to organisms that reside in or on the sediments, or feed either directly on the sediments or on benthivorous organisms. It is documented that heavy metals, particularly copper, lead, manganese and zinc as well as hydrocarbons, are the major contaminants entering streams in association with the suspended sediment load (Ellis, 1986; Sartor & Boyd, 1972). Indeed, a number of studies have concerned themselves with sediment contamination as a cause of biological impairment (Payne, 1989; Maltby *et al.*, 1995a, 1995b; Perdikaki & Mason, 1999). Perdikaki & Mason (1999) recommended the study of metal contaminant concentrations in sediments to investigate possible pollution events as the contents are generally above detection limits, which is often not the case with water samples. These samples provide a contaminant sample integrated over time, eliminating the problem of erratic fluctuations in metal concentrations often observed in water (ibid). Seasonal sampling should indicate whether there is a temporal and / or spatial variation in the sediment metal concentration.

Metallic micropollutants are mainly linked to finer sediments with the highest concentrations typically associated with street surfaces and car parks. Unsurprisingly therefore, heavy metal concentrations increase with decreasing receiving water sediments surface particulates size, (Wilber and Hunter, cited in Herricks & Jenkins,

1995). Consequently, sediments that should be targeted as potential problem sources during receiving water assessment are the small-grained depositional sediments (Burton & Pitt, 2002). The reasons for this are summarised by Power & Chapman (1992):

- various toxic contaminants that are found in barely detectable amounts in the water column can accumulate in sediments at much higher levels;
- sediments can serve as both a sink for contaminants and a source of contaminants to the water column and organisms;
- sediments integrate contaminant concentrations over time, whereas water column contaminant concentration are much more variable and dynamic;
- sediment contaminants (in addition to water column contaminants) affect bottom dwelling organisms and other sediment-associated organisms, as well as the organisms that feed on them;
- sediments are an integral part of the aquatic environment that provide habitat, feeding, spawning and rearing areas for many aquatic organisms.

In contrast to agriculturally impacted sediments [pesticides, nutrients], heavy metals and organic micropollutants are of more interest in urban watercourses. Organic micropollutants encompass chlorofluorocarbons (CFCs), polycyclic aromatic hydrocarbons (PAHs), phthalate esters (PEs), polychlorinated biphenyls (PCBs) and pesticides such as dichloro-diphenyl-trichloroethane (DDT). Research into organic chemicals has focused primarily on compounds that are toxic to plants, animals and humans, and those that are persistent, causing bioaccumulation in organisms and along food chains, particularly PCBs, CFCs and pesticides (Beasley & Kneale, 2002).

Although having received less attention, PAHs, which are common in the urban environment, are likely to be the main group of organic contaminants, with the greatest potential toxicity within urban stormwater discharges (Beasley & Kneale, ibid.). Metals, as a group, were by far the most prevalent priority pollutant constituent found in urban runoff by the NURP studies (U.S. EPA, 1983) with the most commonly detected metals: lead, copper and zinc present in 91% of samples. Road runoff alone, is estimated to contribute between 50 and 70% of instream heavy metal contamination (Ellis *et al.*, 1986). The importance of sediments in the environmental quality of water bodies is without question (Cole *et al.*, 2003), who

concluded that there was far greater utility in assessing sediment contamination than that contained in water column sediment. This is because suspended sediments themselves are not recognised as an environmental receptor supporting anything we would want to protect, in contrast to bed sediment or the water column which supports living organisms (Cole *et al.*, ibid.). In any event, the volumes of water required to yield sufficient volumes of sediment for analysis would have been prohibitive, as has been reported elsewhere (May *et al.*, 2003). Some 40 litres would have been required at each site (based on mean sediment concentrations of 15 mg l^{-1}) to provide enough material to run tests for metals alone. Consequently the study incorporated the collection and analysis of benthal sediments from the brook for PAHs and heavy metals.

PAHs

PAHs are a group of over 100 different chemicals that are formed during the incomplete combustion of petrol in vehicles, creosote coating on wood such as telephone poles or bridge and dock pilings, incomplete burning of coal, oil and gas, domestic waste, or other substances such as tobacco, at temperatures between 650° - 900° C. They are ubiquitous in the environment, are persistent and have a high affinity for biological lipids, producing direct or long-term harmful effects and as such, are classified as List 1 substances under the Dangerous Substances Directive (CEC, 976). Certain low molecular weight PAHs are directly toxic to aquatic life and high molecular weight PAHs are highly carcinogenic to animals including humans (Law *et al.* 2002, cited in SEPA, 2003a) when metabolised to forms which bind to DNA. Indeed, PAHs represent the largest class of suspected carcinogens (Bjőrseth & Ramdahl, 1985 cited in van Metre *et al.* 2000). In aquatic systems, PAHs tend to become adsorbed to sediments but if disturbed can become resuspended. It is likely that lower weight PAHs are most readily released from sediment into this dissolved form (DEFRA, 2002).

The largest analysis of organic chemicals in storm water was the Nationwide Urban Runoff Programme (U.S. EPA, 1983) which looked for 106 organics of which, 63 were identified in the stormwater of participating cities (Makepeace *et al.*, 1995). PAHs are usually found as a mixture containing two or more of these compounds. The NURP Priority Pollutant Study concluded that certain PAHs were a concern in storm water, finding *fluoranthene, napthalene, phenanthrene* and *pyrene* as the most common, occurring in 10 to 12% of samples. Although in overall terms, PAH emission

in the UK has reduced since the 1960s, the environmental burden is still rising as degradation of sediment bound PAHs is gradual (SEPA, 2003a). Notwithstanding this improvement, 16,000 tonnes of used lubricating oil alone is released into the UK environment every year (SEPA, 2003b) and road runoff alone is estimated to contribute to 10 - 20% of PAH contamination in receiving streams (Ellis *et al.*, 1986, cited in SEPA, 2003a). Studies have identified that 86% of hydrocarbons were associated with particulate matter (MacKenzie & Hunter, 1979) whilst others (Hoffman *et al.*, 1982), have suggested that up to 93% of hydrocarbons are associated with particulate matter, illustrating the potential of sediments in exposure of PAHs to aquatic life. It would also seem likely that the impact to receiving waters from thermally and pyrogenically derived PAHs will, due to predicted traffic growth over the next decade, increase in severity. Coring studies have shown that concentrations of PAHs have been increasing over the past 20 - 40 years correlating strongly with increasing vehicle use even in catchments that have not undergone substantial changes in urban land-use levels since the 1970s (van Metre *et al.*, 2000). Prima facie evidence appears to indicate PAHs in reduced macroinvertebrate diversity below inputs of road runoff (Maltby *et al.*, 1995a) whose fractionation studies indicated that most of the observed toxicity was due to the fraction containing PAHs. As with heavy metals, PAHs preferentially adsorb to fine particulate matter. However, other studies have been less conclusive (Bennett & Cubbage, 1992), and there still appears to be a general paucity of research in this area.

Metals

Cadmium and its compounds are listed in the Dangerous Substances Directive (76/464/EEC) as List 1 substances, while beyrillium, copper, chromium, lead, nickel, silver and zinc are List 2 substances. Fifty-nine of the elemental metals can be classified as "heavy metals", of which, 17 are considered both very toxic and available in places at concentrations that exceed toxicity levels (Novotny & Olem, 1994). Table 6.1 outlines the diffuse sources of trace metals in water. Although trace metals occur naturally at low levels, nine of these are being mobilised into the environment by man at rates greatly exceeding those of natural geological processes (Novotny & Olem, ibid). Three of these; copper, lead and cadmium are characterised by their association with organic matter of which copper is the major aquatic toxic metal in stormwater, usually correlated to the intensity of vehicular traffic (Dannecker *et al.*, 1990). Investigation of

sediment cores in Brazil by Neto *et al.* (Cited in Clark *et al.*, 2000), indicated that the increase in sediment metals concentration occurred at approximately the same time that rapid urbanisation began in the watershed.

Pathway	Contaminants	Sources
Domestic sewers	B†	Detergents
	Pb†, Cu†, Zn†	Supply pipes and soldered joints
	Zn	Cosmetics
Roads	Cd*, Zn, Pb, Ni†	Tyres
	Pb	Petrol (ceased in UK as of 01/01/00)
	Pt	Catalytic converters
	Cu	Brakes
	Ni	Diesel
	Cr†	Vehicle plating
Industrial estates	Cd	Electrical cables
	Cr	Tanneries, chromite works
Agriculture	Cu, TBT*	Fungicides to land
	Cd	Phosphate fertilisers to land
	Zn, Cu	Animal manure to land
	Pb, Zn, Cu, Cd and others	Sewage sludge to land

Table 6.1: Diffuse sources of trace metals in water. Source: SEPA, 2003
* List I substance Dangerous Substances Directive (76/464/EEC)
† List II substance Dangerous Substances Directive (76/464/EEC)

6.3 Sampling method

Appropriate sampling of instream sediments is essential to ensure that the sediment depth sampled for analysis corresponds to that affecting or responsible for, organism exposure to contaminants. SEPA (2003) recommend analysis of the top layer of sediment (0-2 cm), the most common depth obtained (Burton & Pitt 2002). Benthic macroinvertebrates live within the upper layers of streambed sediments in constant direct contact with contaminants, receiving prolonged exposure via gill cell osmosis and ingestion (Beasley & Kneale, 2002) hence the requirement to sample this strata. For metals and toxic contaminants, a sample volume of 500g, collected into a glass jar with inert lid is recommended by Naden *et al.* (2002) to provide sufficient mass to yield sufficient sub-samples of 1 to 3g per analysis, and allow for repeat analysis if required. Burton & Pitt (2002) meanwhile, recommend a sample volume of between 1 and 3 litres of sediment. Other studies such as that conducted by Maltby *et al.*, (1995a) collected triplicate samples of approximately 20g from the top 2 cm of sediment. It appeared therefore, that trial and error was required to determine the optimum volumes required

for analysis. Guidelines for the physical sampling and analysis of river bed sediments have been developed by ISO, with sampling of bottom sediments covered by ISO 5667-12, (1995). To avoid conflicting results and obtain an average picture, multiple samples of sediment (approx 1 kg in total) were collected randomly at each site from the top 5 cm of sediment, using a trowel and in sequence from downstream to upstream. Each composite sample was stored in high-density polyethylene containers for metal analysis. The process was repeated with samples stored in amber glass jars for PAH analysis. This method produces minimal disturbance of the streambed, low risk of contamination and minimal loss of the finest particles that generally possess the highest metal concentrations (Beasley & Kneale, 2003). The method of preservation used was that outlined in British Standard 6068-6. 15: 1999.

6.4 Analysis

PAHs

The technique used to extract polycyclic aromatic hydrocarbons from the sediment samples followed the U.S. Environmental Protection Agency's Method 3540C (U.S. EPA, 2003). Cleanup procedure followed that of the U.S. EPA Method 610 (U.S. EPA, 1986), with extracts concentrated to 1 ml, prior to analysis by HPLC. The sediment extracts were analysed for the following 15 selected PAHs:

Low-molecular-weight PAH

- Napthalene
- Acenaphthylene
- Acenaphthene
- Fluorene
- Phenanthrene
- Anthracene

High-molecular-weight PAH

- Fluoranthene

- Pyrene
- Benz[a]anthracene
- Chrysene
- Benzo[b]fluoranthene
- Benzo[k]fluoranthene
- Benzo[a]pyrene
- Dibenzo[a,h]anthracene
- Benzo[g,h,i]perylene
- Indeno[1,2,3-c,d]pyrene

Source: SEPA (2003b)

The list contains the PAHs employed by the Scottish Environmental Protection Agency for their Diffuse Pollution Initiative (SEPA, 2003b) which includes the 13 PAHs listed by Burton & Pitt, (2002) for which reliable sediment quality guidelines are available. The PAH analysis was carried out via positive electron ionisation using a Hewlett Packard 5890-A gas chromatograph. Samples (1 ml) were introduced by syringe, with the following operating parameters: a 1 - µl shot was injected with the source temperature at 200^0C and a solvent delay period of 4 minutes; the initial oven temperature was 80^0C, increased at 15^0C / min to 220^0C, after which the temperature was increased at 10^0C / min to 280^0C, followed by a further increase of 5^0C / min to 300^0C, the oven was kept at this temperature for 10 minutes with a total run time of 30 minutes. Calibration was achieved using a RESTEK™ SV Calibration Mix (2000 µl / ml in methylene chloride), at concentrations of 1, 12.5, 25 and 50 µl / ml. An internal standard of 25 µl / ml was introduced to each sample using a RESTEK™ Anthracene D 10 Mix.

Metals

Whole samples were dried as per BS 6068-6 (British Standards Institute, 1999), at 60^0C until the mass reached constancy. Samples were then sieved through an acid-washed 2 mm nylon mesh to remove large clasts, vegetation, invertebrates and litter and

then ground in a Pascall Engineering™ pestle and mortar to pass a 125 μm sieve. (No standard method exists for particle size reduction prior to chemical digestion).

Sediment was prepared for metal analysis by coning and quartering the dried sediment, of which 0.2 g was placed into acid-washed glass test tubes into which 10 ml of 70 % Aristar nitric acid was added. The tubes were then placed in a preheated Grant™ block digester at 80^0C for 2 hours. On cooling, the samples were transferred to acid-washed volumetric flasks and made up to 50 ml with distilled water ready for analysis by ICP-OES. For ICP-MS analysis, 2 ml was taken from each volumetric flask and made up to 50 ml in another volumetric flask to avoid overloading of the more highly sensitive instrumentation.

In all cases, triplicate samples were analysed for each site with blank samples incorporated into the testing regime (i.e. reagent without addition of dried sediment). All glassware used in the preparation of samples were cleaned in a 10% nitric acid bath overnight, followed by three rinses in deionised water. As with the water samples, metals were analysed using a Hewlitt Packard Spectroflame Model-P Optical Emission Spectrometer and an Agilent 4500 Mass Spectrometer. The metals determined in these analyses were Ag, Al, Be, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn.

6.5 Results

In the UK there are presently no sediment quality guidelines (Apitz *et al.*, 2003). Similarly, there are currently no published guidelines in the UK with which to assess the quality of marine sediments (Hutchison Port UK Ltd, 2003). English Nature (2001) have stated the need to set sediment quality guidelines for the protection of water, regarded as implicit in the Water Framework Directive, which defines an environmental quality standard as; "the concentration of a particular pollutant or group of pollutants in water, sediment or biota which should not be exceeded in order to protect human health and the environment". Certainly drivers exist for the setting of standards, such as the control of priority substances and the need to achieve good ecological status enshrined in the WFD. In addition, Apitz *et al.*, (2003) suggest that a mismatch between ecological and chemical water quality could serve as a trigger for sediment investigation.

In the absence of standards, the results from the sediment analysis are presented in this section in comparison with the Canadian Sediment Quality Guidelines

(Canadian Council for Ministers of the Environment, 2001). As the guidelines are based on empirically determined relationships between pollutants and biota from North America, their exceedance or otherwise by the study results need to be treated circumspectly. Nonetheless their interpretation can serve to highlight potential areas of concern.

PAHs

Contaminated sediments contained between 2592 and 25,961 μg total hydrocarbons / kg dry wt. Peak total concentrations of PAHs at sites d and g, (15,247 & 25,961 respectively) compared with the highest concentrations (total PAH >10,000 μg kg^{-1} dry weight) reported by the 1998 National Monitoring Programme Survey of the Quality of UK Coastal Waters (Marine Pollution Monitoring Management Group, 1998) in the highly industrialised estuaries of north-east England, particularly in muddy sediments from the Rivers Tyne and Wear. Within the study catchment, the dominant PAHs at the most contaminated site (*g*) were fluoranthene (5591 μg / kg wet wt.), pyrene (4726 μg / kg wet wt.) and phenanthrene (3812 μg / kg wet wt.), comparable to levels found in sediments contaminated by M1 motorway runoff (Maltby *et al.*, 1995a). The dominance of these three high molecular weight PAHs mirrors the findings of Shinya *et al.* (2000), who found from investigations into pollutant concentrations from road drains, that phenanthrene, pyrene and fluoranthene constituted approximately 50 % of the total PAHs determined in each sample. Individual PAHs, notably benzo[g,h,i]perylene, pyrene and fluoranthene exceeded 80 % of the highest values recorded in the National Monitoring Programme Survey of the Quality of UK Coastal Waters (Marine Pollution Monitoring Management Group, 1998). Total PAHs at site g, equated to 73 % of the highest value reported by the above study from the River Tyne at Hebburn [35,400 μg / kg dry weight]. Additionally, benz[a]anthracene and chrysene were elevated at the most downstream site (2483 μg / kg, and 2426 μg / kg respectively). Total PAHs peaked at sites *d* and *g* with concentrations of 13453 and 25961μg / kg dry wt. respectively. Of the twelve PAHs for which PELs are calculated, 8 were exceeded at site *d* and *g* (table 6.2). Table 6.3 compares the Canadian Sediment Quality guidelines with the values for Charlton Brook. Individual site values for sediment PAH concentrations can be found in Appendix VIII.

Location of individual PAHs in exceedance of Canadian Sediment Quality Guidelines Probable Effect Level (PEL ●)					
	a	d	e	f	g
Acenaphthene		●			●
Acenaphthylene					
Anthracene	●	●	●	●	●
Benz[a]anthracene		●			●
Benzo[a]pyrene					
Chrysene		●			●
Dibenzo[a,h]anthracene	●	●			
Fluoranthene		●			●
Fluorene					●
Indeno[1,2,3-cd]pyrene					
Naphthalene					
Phenanthrene		●			●
Pyrene		●			●

Table 6.2: Sites where PAH levels exceeded PEL guidelines.

Compound	Canadian Sediment Quality guidelines (µg / kg dw)		Charlton Brook range (µg / kg dw) Average levels in parenthesis
	ISQG[1]	PEL[2]	
Acenaphthene	6.71	88.9	3.6 - 181 (69.1)
Acenaphthylene	5.87	128	3.1 - 29.3 (14.3)
Anthracene	46.9	245	602 - 2013 (1125)
Benzo[a}anthracene	31.7	385	0 - 2483 (677)
Benzo[k]fluoranthene	--	--	0 - 1843 (907)
Benzo[b]fluoranthene	--	--	0 - 1650 (855)
Benzo[a]pyrene	31.9	782	--
Benzo[g,h,i]perylene	--	--	0 - 1615 (585)
Chrysene	57.1	862	0 - 2426 (826)
Dibenzo[a,h]anthracene	6.22	135	0 - 832 (305)
Fluoranthene	111	2355	0 - 5592 (1818)
Fluorene	21.2	144	14.5 - 211 (79.2)
Indeno[1,2,3-cd]pyrene	--	--	0 - 962 (267)
Naphthalene	34.6	391	8.9 - 79.6 (42.5)
Phenanthrene	41.9	515	144 - 3812 (1242)
Pyrene	53	875	279 - 4726 (1708)
PAH (total)	--	--	2592 - 25961 (10522)

Table 6.3: Comparison of Charlton Brook PAH levels with sediment quality guidelines.

1: ISQG: Interim freshwater sediment quality guidelines (dry weight).
2: PEL: Probable effect level (dry weight).

PAH ratios

The ratios of different PAHs were used to infer the likely source of PAH contamination. For example, phenanthrene and anthracene are structural isomers, but anthracene originating from oil spills degrades more rapidly than from combustion. This is not the case for phenanthrene. Therefore, a low Phe / Ant ratio (<10) suggests that a greater proportion of the PAH contamination originates from pyrolitic sources (Wilson *et al.*, 2003). Fluoranthene and pyrene ratios can similarly be utilised with simultaneous study of the ratios allowing for the definition of two different classes of sediments: Phe / Ant (>10) and Flu / Pyr (>1) for petrogenic inputs and Phe / Ant (<10) and Flu / Pyr (<1) for the dominance of pyrolitic sources (Budzinsky *et al.*, 1997, cited in Dahle *et al.*, 2003). The phenanthrene / anthracene & fluorene / pyrene ratios occurring in the stream sediment samples are shown in (figure 6.1), suggesting that combustion sources (vehicle engines) were more widespread and present within the catchment in greater quantities than oil spill sources.

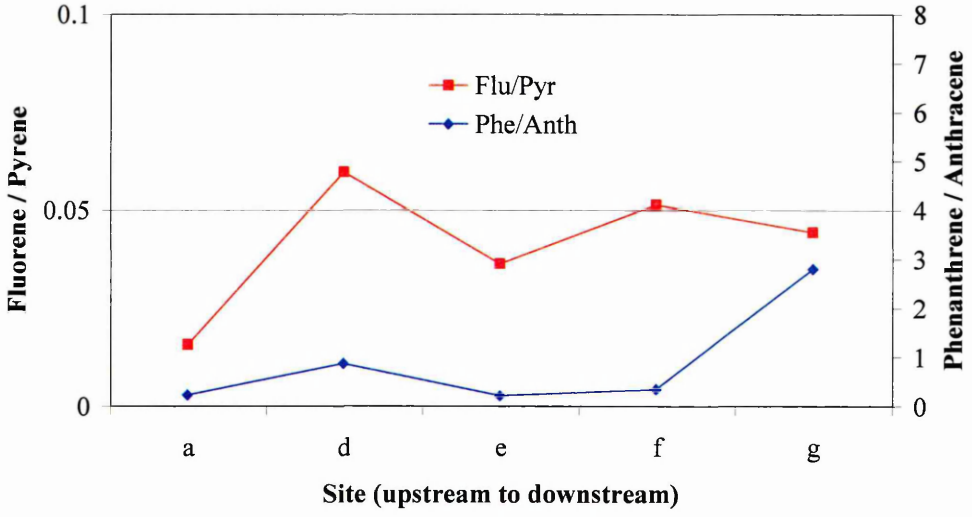


Figure 6.1: comparison of PAH ratios by site.

Another method of determining the likely source of PAHs is to compare the uncombusted and combusted species. Uncombusted sources such as petrol spills, contain predominantly two and three-ringed compounds (low molecular weight), whereas combustion, such as vehicle exhaust contains predominantly four and five-ring

species (van Metre *et al.*, 2000). Concentrations within the study site show that high molecular weight PAHs are between 1.7 and 3.6 times greater than low molecular weight PAHs. Figure 6.2 shows the comparison of the total concentration for these two groups. This conforms to the observations reported by Walker *et al.*, (1999), that urban runoff PAH distributions contain fewer low molecular weight PAHs and tend to be associated with suspended solids in the runoff.

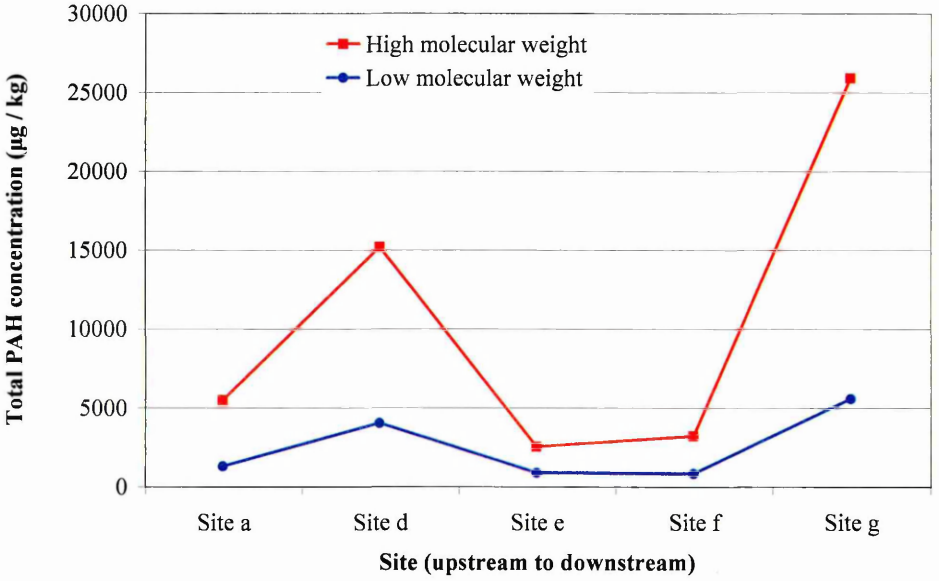


Figure 6.2: Comparison of total high and low molecular weight PAHs.

Summary PAHs

All sites within the brook exceeded one or more PEL levels, with sites *d* & *g* containing eight PAHs in excess of the PEL, defined as the level above which adverse effects are expected to occur frequently (Environment Canada, 2004). The PEL represents the lower limit of the range of chemical concentrations that are usually or always associated with adverse biological effects (Canadian Council of Ministers of the Environment, 1995). Sediments with concentrations of one or more chemicals that fall within this range of concentrations should be considered to be of the highest priority for appropriate management actions to improve sediment quality and restore the desired level of protection, if necessary (ibid.) Conversely, sediments with concentrations equal to or lower than the ISQGs, are considered to be of acceptable quality (Canadian

Council of Ministers of the Environment, 1999). Sediments with measured chemical concentrations between the ISQG and the PEL are considered to represent potential hazards to exposed organisms (ibid.).

Metals

Table 6.4 below, displays the metals exceeding sediment quality guidelines. All those indicated exceed the Canadian ISQG level with the exception of chromium at site *d*, which exceeded the severe effect level.

	Site a	Site d	Site e	Site f	Site g
Ag*		•	•	•	•
Cd		•	•		
Cr		••			•
Cu					
Fe		•	•	•	
Mn					
Ni					
Pb		•		•	•
Zn					

Table 6.4: Sediment guideline exceedance at sampling sites. * Indicates threshold determined by Cubbage *et al.* (1997). •Indicates exceedance of ISQG and Lowest Effect Level, ••Indicates exceedance of Severe Effect Level

As can be seen from table 6.4, silver exceeded the lowest apparent effect threshold determined by Cubbage *et al.*, (1997). From site *d* onwards all levels are in excess of the standard. Chromium exceeds the standards at sites *d* and *g*. Iron and manganese levels are high within the catchment, in exceedance or close to, the sediment quality standards; possibly as a consequence of the area's geology and buoying the total sediment metal at each site. At site *g*, manganese exceeds the severe effect level. Figure 6.3 illustrates the total recoverable metal at each site for those metals listed within the sediment quality guidelines, of which iron was the greatest single contributor. High levels of iron are not unusual and stream sediment concentrations of 10 - 20% iron and up to 2% manganese have been reported elsewhere in the literature (Abesser & Soulsby, 2002).

Sediment quality guidelines compared to Charlton Brook values (mg / kg)				
Metal	Canadian Sediment Quality Guidelines for the protection of aquatic life		Sediment quality guidelines from other sources (In Roose, 2002)	Charlton Brook Sediment levels (range). Average values in parenthesis. Bold values exceed guidelines.
	ISQG[1]	PEL[2]		
Ag	--	--	4.5[a]	**3.4 - 9.53 (5.5)**
Al	--	--	--	3390 - 4820 (4071)
Be	--	--	--	0 - 0.36 (0.12)
Cd	0.6	3.5	0.99[b]	0 - 0.56 (0.21)
Cr	37.3	90	43[b]	**11.6 - 284 (81.4)**
Cu	35.7	197	32[b]	3.9 - 22.4 (13.1)
Fe	--	--	20000[c]	**12517 - 27092 (20127)**
Hg	0.17	0.486	0.56[a]	**22.5 - 46.4 (30.8)**
Mn	--	--	1800[a]	242.3 - 1242 (658.1)
Na	--	--	--	800.5 - 1242 (1041.6)
Ni	--	--	46[a]	7.4 - 12.5 (10.1)
Pb	35	91.3	36[b]	**14.9 - 50.3 (30.8)**
Zn	123	315	121[b]	26.7 - 49.3 (35.2)

Table 6.5: Comparison of Charlton Brook sediment metal levels with known standards.

1: ISQG: Interim freshwater sediment quality guidelines (dry weight).
2: PEL: Probable effect level (dry weight).
3: Lowest Effect Level (dry weight).
4: Severe Effect level (dry weight).
a: Lowest Apparent Effect Threshold (Cubbage *et al.*, 1997).
b: Consensus-based Threshold Effect Concentrations (MacDonald *et al.*, 2000).
c: Lowest Effect Level (Persaud *et al.*, 1993)

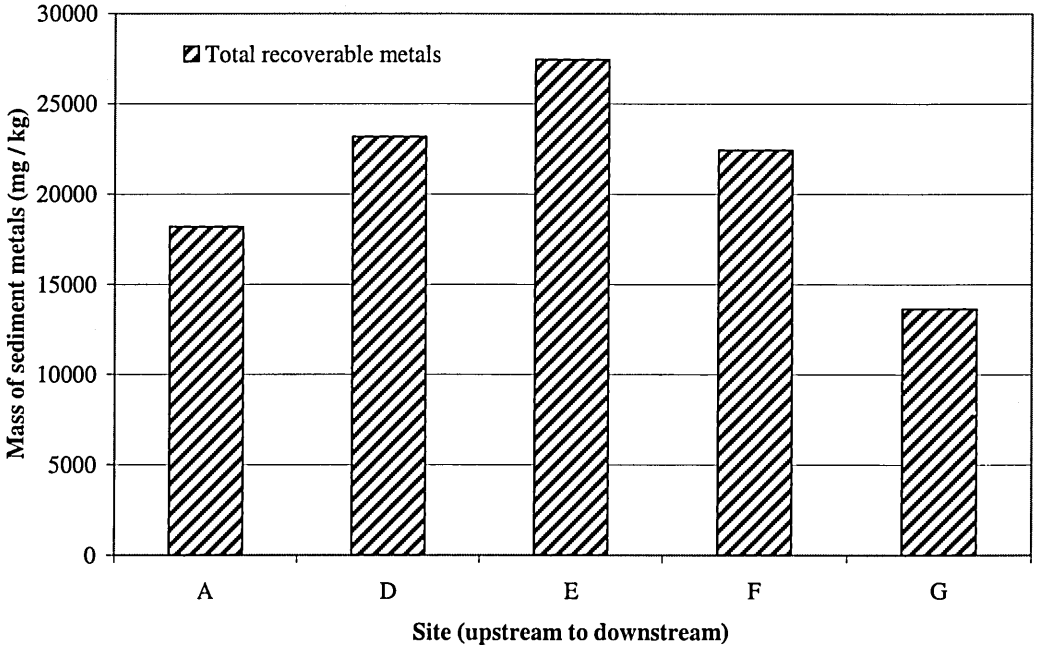


Figure 6.3: Total recoverable metal at each site as dry weight.

6.6 Background sources

The geology of the study site may well be responsible for the occurrence of certain sediment metal levels contained in table 6.5. The geology underpinning the study site is coal measures, shales and sandstones. Natural dust, the suspended proportion in river water and the detrital silicate fraction in coal is often comparable to shales in chemical composition (Merian, 1991). In addition to this silicate fraction, coal has accumulated several elements via the physiological processes of its parent flora such as magnesium and zinc and through diagenesis of sulphides (cadmium, copper, iron and silver for example). In freshwater sediments, sorption sites are provided by organic carbon, clays and hydrous oxides of iron and manganese. Hydrous iron strongly adsorbs chromium with manganese adsorbing nickel and calcium phosphate (also present in sediments) adsorbing cadmium, lead and other metals (Salomons, 1995). Iron oxidation has been found to neutralise heavy metals such as lead, mercury, and uranium by transforming them into insoluble forms that are less likely to leach into groundwater or be absorbed by plants and transmitted through the food chain (Zhang, 2003). The scope of this thesis does not extend to the analysis of the sites geo-chemical make up but for ease of reference, a table listing typical concentrations of elements in shales, sandstones and coal has been included (table 6.6).

Metal	Shale	Sandstone	Coal (hard)[1]
Ag	0.07	0.25	0.44
Al	82000[3]	--	--
Be	--	--	2.6
Cd	0.22	0.05	1.8
Cr	39	35	13
Cu	39	30	16
Fe	48000[2]	--	9000
Hg	0.18	0.29	0.36
Mn	850	460	156
Na	23000[3]	--	--
Ni	68	9	22
Pb	23	10	46

Table 6.6: Concentrations in ppm for metals in shale, sandstone and coal.
Source: Alloway & Ayres, 1991. Except [1& 2] : Merian, 1991. [3]: Crustal abundance, source: http://www.webelements.com

Whilst aluminium is the third most abundant element in the environment, the naturally occurring forms are usually stable and do not interact with the biological processes which go on in living organisms. Under acidic conditions, aluminium is liberated from clays at pH 4.0 (Alloway & Ayres, 1997) however, aluminium is released from rocks and soils in a soluble form which can be absorbed by plants and animals. It is abundant in feldspars and clay minerals and as Al_2O_3 in shales. Sodium is the sixth most abundant element and is widely distributed. However, because of its high reactivity is not found naturally in its elemental state.

6.7 Mean PEL-quotient interpretation of metals and PAHs

A method for ranking the sampled sites was carried out by the author using the method proposed by the Contaminated Sites Management Working Group, (CSMWG, 2003) under the auspices of the Government of Canada. The method is based on Long and MacDonald's (1997) PEL-quotient approach, using sites' mean PEL quotients and/or number of PELs exceeded to determine relative site priorities, based on the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (CCME, 1998). The degree by which guidelines are exceeded, is estimated by dividing the concentration of each chemical present in the sediment by its corresponding PEL to obtain a PEL-quotient. The PEL-quotients of the various chemicals in the sample are then summed and normalised according to the number of PEL-quotients in the sample. The two endpoints (the normalised PEL-quotient and the number of guidelines exceeded) then serve to prioritise sites of concern (Environment Canada, 2004). The mean PEL-quotient is derived thus:

$$\text{Mean PEL-Quotient} = \frac{\sum \frac{m}{p}}{q}$$

Where m is the measured contaminant concentration, p is the probable effect level and q is the number of PEL-quotients calculated. Pollutant levels below the limit of detection are not included.

Sediment Parameter	Measured Concentration	$CCME_{98}$ Guideline Limit (PEL)	Mean PEL Quotient Derivation Steps		
			Step 1: Derive PEL quotients	Step 2: Sum tde PEL quotients derived in Step 1	Step 3: Derive mean PEL quotient for tde sample
Cadmium	1.4 mg/kg	4.2 mg/kg	(Measured contaminant concentration / PEL) 1.4 / 4.2 = 0.33	0.33 + 3.01 + 2.18 + 1.87 + 0.30 + 0.05 + 0.10 + 0.00 + 0.32 = 8.16	(Sum of PEL quotients / the number of PEL quotients calculated in Step 1) 8.16 / 9 = 0.91 Sample #1 mean PEL quotient is 0.91
Copper	325 mg/kg	108 mg/kg	325 / 108 = 3.01		
Lead	244 mg/kg	112 mg/kg	2.18		
Zinc	508 mg/kg	271 mg/kg	1.87		
Benzo(*a*)pyrene	232 µg/kg	763 µg/kg	0.30		
Dieldrin	0.2 µg/kg	4.3 µg/kg	0.05		
Fluoranthene	145 µg/kg	1494 µg/kg	0.10		
PCBs, total	0.08 µg/kg	189 µg/kg	0.00		
Pyrene	454 µg/kg	1398 µg/kg	0.32		

Table 6.7: Sample method for deriving PEL-quotients.
Source: Contaminated Sites Management Working Group, 2003.

This approach has been shown to have a high reliability of predicting impairment with the probability of observing toxicity shown to be a function of both the number of substances exceeding the various guidelines as well as the degree to which they exceed the guidelines. (CSMWG, 2003). Table 6.7 summarises an example for the method of calculation.

Relative site priorities are determined by the matrix shown in table 6.8, and contains the stated need for further action indicated by the five classes of hazard. Its purpose is to provide an evaluative framework for ranking marine and aquatic sites within general categories of concern, thereby indicating the need for further action. It is not intended to provide a general or quantitative risk assessment; rather, it is to be used solely as a tool for screening-level identification and prioritisation of contaminated marine and aquatic sites (CSMWG, 2003). As such, it is not an absolute predictor of effects and the remediation required to nullify them. As stated by the CSMWG (ibid.), further investigations or assessments may be required to provide supplemental information and to confirm the existence and extent of predicted toxicity, given the modifying factors that may affect toxicity, referred to in previous reports, e.g. synergism / antagonism of different pollutants, particle sizes, background concentrations etc. However, the predictive ability of these consensus-based threshold and upper effect levels in

estimating toxicity and non-toxicity has been found to range from 71% to 100% for the various substances being tested (MacDonald *et al.*, 2000). Figure 6.4 below illustrates the relative mean PEL-quotients by site.

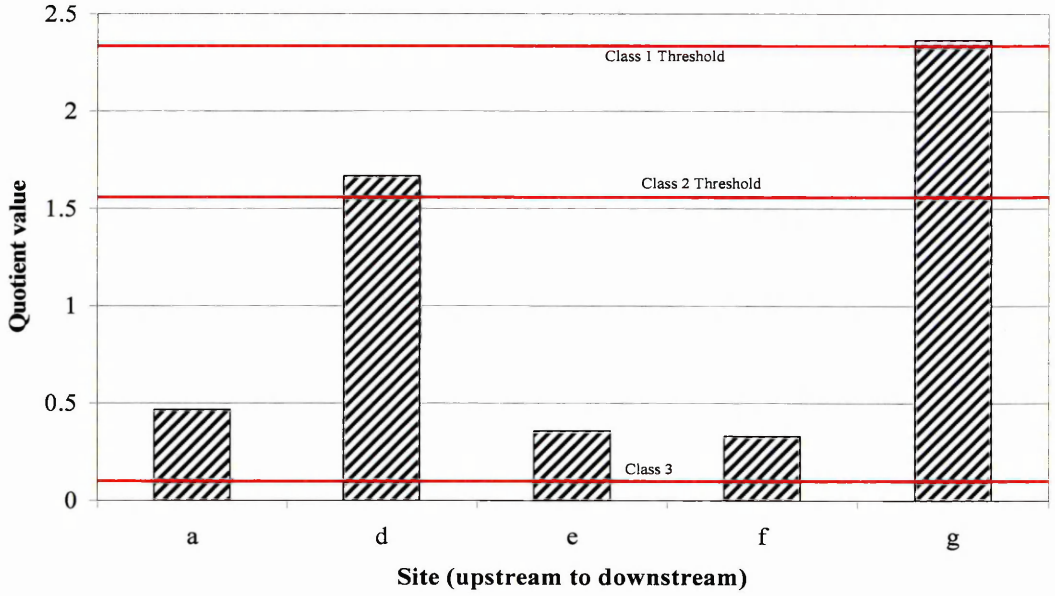


Figure 6.4: Relative mean PEL-quotient values for sediment samples by site, with indicated threshold values for different classes of potential toxicity.

PEL-quotient values varied throughout the watercourse with all sites having the potential for adverse biological effects. The PEL approach has been shown to have a high reliability of predicting impairment with the probability of observing toxicity shown to be a function of both the number of substances exceeding the various guidelines as well as the degree to which they exceed the guidelines. (CSMWG, 2003). Significant differences between sites *a*, *f* and *g* in relation to sites *d* and *g* were confirmed in relation to PEL quotient levels. The differences between sites *d* and *g* and between *a*, *e* & *f* were not significant.

Table 6.8 illustrates the determination of hazard ranking based on mean PEL-quotient and the number of PEL / ISQG exceedencies. Appendix IX contains the actions suggested as being required for each of the rankings.

Relative Priority Ranking	Determination of Relative Priority Ranking	Hazard Ranking Score
Highest Priority Sites	Mean of (mean sample PEL quotients) > 2.3 **and/or** 21 or more PELs exceeded	**1**
Medium-high Priority Sites	Mean of (mean sample PEL quotients) 1.51 - 2.3 **and/or** 6-20 PELs exceeded	**2**
Medium-low Priority Sites	Mean of (mean sample PEL quotients) 0.11 -1.5 **and/or** 1-5 PELs exceeded	**3**
Lowest Priority Sites	Mean of (mean sample PEL quotients) < 0.1 **and/or** No ISQGs exceeded	**N**
	Insufficient data to adequately determine site sediment quality	**I**

Table 6.8: Site priorities determined by PEL-quotients and / or PEL / ISQG exceedencies.
Source: Contaminated Sites Management Working Group, 2003.

Comparison of the PEL values and the number of contaminants within each sample that exceed the individual PEL and ISQG standards draws a significant conclusion. All sites have the potential for adverse biological effects, falling within 'Class 3' in the case of sites *a, e & f*, 'Class 2' in the case of site *d* and 'Class 1' in the case of site *g* (table 6.8). Class 3 sites will 'typically be those with localised areas of low to moderate contamination' and Class 2 sites 'will typically be those with localised areas of moderate to high contamination...with impacts to biological components indicated'. Class 1 sites will typically have widespread and high levels of sediment contamination, and measured or observed impacts on species composition / diversity will have been documented. (CSMWG, 2003). MacDonald *et al.* (2000), in their evaluation of sediment quality guidelines, found that out of 125 sediment samples with a mean PEC (PEL) quotient of greater than 1.5, 118 were found to be toxic, based on the results of various freshwater toxicity tests; a predictive ability of 94%. Similarly, 92% of sediment samples with a mean PEL quotient of > 1.0 (132 of 143) were found to be toxic to one or more species of aquatic organism. Of the 174 samples with a mean PEL of < 0.5, 30 were found to be toxic to sediment-dwelling organisms; a predictive ability of 83%.

By plotting the incidence of toxicity against the ranges of mean PEC-quotients, MacDonald *et al.* (2000) also demonstrated that mean PEL-quotient is highly correlated

with incidence of toxicity (r^2 = 0.98). The resultant equation ($Y = 101.48\ (1\text{-}0.36^X)$), where X is the mean PEL-quotient, is used to estimate the probability of observing sediment toxicity for any mean PEL-quotient. Not surprisingly, sites d and g confirmed their relative likelihood of toxicity with probabilities of 83 and 92% respectively. Sites *a*, *e* & *f* meanwhile, show a similarly low likelihood of toxicity, (39, 31 & 29% respectively), suggesting that for *e* & *f* at least, other factors may be at work given their reduced invertebrate richness, diversity and evenness along a continuum of decline from upstream to downstream.

Interestingly, all sampled sites have a higher proportion of high to low molecular weight PAH ratios ranging from 1.8 : 1 at site *e* to 3.6 : 1 at site *g*. In clean aquatic environments, half lives for PAHs with 2 to 3 fused benzene rings in their structure typically range from 3 to 120 days, whilst compounds with 4 rings have half lives of around 500 to 1100 days (Environment Agency, 2002).

6.8 Summary

Overall, the level of PAH contamination within Charlton Brook is unlikely to improve. Traffic volumes are forecast to grow from 488 billion vehicle km in 2000 to 688 billion vehicle km a year in 2025 in the UK (Transport Research Laboratory, 2002). Increasing concentrations of PAHs in reservoirs and lakes have been studied by Van Metre *et al.*, (2000), who suggest that the trend of increasing PAH concentration in sediments is indicated by increasing vehicle use. Analysis of the determined PAHs supports this view.

Whilst used primarily as a guide, breakdown of the PEL-quotients into their component parts, shows that potential for sediment toxicity at the different sites was largely driven by the PAHs. Generally, the metal species exceeded the lower of the two guidelines, and only within the urbanised portion of the catchment. Site *d* did exceed the PEL for total chromium, by three times the threshold. Mass spectrometry did not differentiate between the trivalent and hexavalent forms which may have helped determine the likely source, given that chromium VI, the most toxic form is typically related to industrial, rather than natural processes.

Chapter 7

Episodic discharges

7.1 Introduction

It is well documented that the bulk of pollutants are transported to watercourses during flood events. These acute discharges typically contain a higher concentration of pollutants than that typified by the general (chronic) quality of a watercourse identified by low flow sampling. As by definition, any pollution discharged into surface water is harmful to aquatic biota or to present or future beneficial uses of water (Novotny & Olem, 1994), determination of storm water quality was included within the study. Seager & Maltby (1989) suggest that the ability of organisms suddenly exposed to pulses of pollutants for short periods of time to acclimate to those rapidly changing conditions is unlikely to be the same as under continuous exposure, citing studies such as that by Thurston *et al.*, (1981) and Brown *et al.*, (1969) who demonstrated that fish were better able to withstand continuous exposure to certain pollutants than to fluctuations with the same mean. Increased toxicity in macroinvertebrates and fish following brief exposure to contaminants has also been reported by others (Abel, 1980; Abel & Gardner, 1986; Pascoe & Shazilli, 1986; Brent & Herricks, 1998). An additional difficulty, is that exposure to a toxin does not always result in death, but may affect fitness or fecundity or effect a change of behaviour. Although laboratory and in-situ exposures are considered to be outwith the scope of this thesis, the prima facie evidence may well suggest that it is indeed the frequent pulses of stormwater pollutants including metals that determine the increasing biological paucity of the river as it flows downstream.

The pollutants under investigation covered the physico-chemical parameters and metals (detailed in previous chapters). Storm prediction was based on information supplied via Metcheck, who provide short, medium and long range weather forecasts, supplemented by the Meteorological Office and BBC Weather web sites. These gave a rough guide as to the likelihood of storm events but typically, proved vague and at times, wholly inaccurate. The Leeds office of the Environment Agency also supplied data on a daily basis. In total, ten storms were sampled for the study.

The following parameters were identified for determination:

DO (% saturation)
Ammonia (mg N/l)
BOD (mg/l)
COD (mg/l)
Suspended solids (mg/l)
pH
Turbidity
Temperature (^{o}C)
Heavy metals: aluminium, beryllium, cadmium, chromium, copper, iron, lead, manganese, nickel, silver and zinc.

Ammonia poses a potential pollution risk to all rivers because of the widespread risk of contamination from sewage or agriculture. Likewise, BOD is an indicator of pollution from organic sources. Both BOD and ammonia concentrations can lead to a lowering of dissolved oxygen, which is essential to aquatic life. Chemical oxygen demand (COD) is considered a vital test for assessing the quality of effluents and waste waters prior to discharge, viz. the amount of organic material in the water. Chemical oxygen demand does not differentiate between biologically available and inert organic matter and is thus a measure of the total quantity of oxygen required to oxidise all organic material into carbon dioxide and water. Sediment can fill gravel spaces eliminating the spawning habitat for some fish and obliterate the habitat for many invertebrates. Suspended sediment can also reduce light penetration, compromising the productivity of invertebrates, which in turn are a major food source for fish. The pH of water affects the solubility of many toxic and nutritive compounds and hence their availability to living organisms. As pH decreases, metals become increasingly soluble and toxic. Temperature controls the metabolic rate and reproductive activity of aquatic organisms. Metabolic rate increases with a rise in temperature, with a commensurate demand for oxygen. However, an increase in water temperature also decreases dissolved oxygen levels as well as providing conditions that favour the growth of disease causing organisms. Metals were chosen on the basis of their inclusion as List 1 substances under the Dangerous Substances Directive (76/464/EEC) as in the case of cadmium. Similarly beryllium, copper, chromium, iron, lead, nickel and zinc were included as List 2

substances under the directive. The remaining metals were chosen due to their inclusion within Canadian sediment quality guidelines and U.S. water quality criteria. In all cases, the metals are indicated as having a potential impact on aquatic life.

At the beginning of a rainfall event the river discharge is low and time will elapse before this discharge rises. This delay is prolonged or shortened by the degree of catchment wetness prior to the storm and the storm intensity itself. Permeable surfaces attenuate rainfall via evaporation, wetting of surface layers and through depression storage, only entering surface waters as runoff when rainfall exceeds the rate at which it can soak into the ground. This proportion of rainfall finding its way to the watercourse is known as *effective rainfall.* As the storm progresses, the proportion of effective rainfall increases and that of lost rainfall decreases. When the rainfall intensity drops below the rate at which the ground can absorb it, the runoff will stop even though it may continue raining. When the groundwater reaches a certain level water will begin to enter surface waters supplementing the recessional limb of the storm.

In contrast to permeable surfaces, drains connected to impermeable surfaces, exhibit a quick response to rainfall with a peak flow occurring a short time after the peak rainfall (2002). In order to establish whether or not pollutant loads within the Brook were associated with the flashy response typically expected from urbanised catchments, modelling of the drainage network was carried out using Hydroworks (Wallingford Software & Anjou Recherche, 1999)

7.2 Hydroworks modelling of the catchment

In this study, Hydroworks was used to produce hydrographs of the downstream rural and downstream urban points in the catchment, based on empirical rainfall data. This enabled comparisons to be made with the rural (permeable) and urban (impermeable) runoff during storm events. Drainage system data was obtained from Yorkshire Water's public asset data held by Chesterfield Town Council. The complete drainage network for Charlton Brook was recorded by hand and reduced in size to a 50-node system. For each of the catchment's networks, the longest branch of connected conduits was calculated and entered into the model as one pipe. The rural tributary sections were broken down into several in-line sections as the model advises against pipe lengths in excess of 500 m. Levels within the drainage network were verified by differential levelling, using benchmarks located throughout the catchment.

The author employed the Constant PR Model within Hydroworks, with empirically derived urban catchment wetness index (UCWI) values for each modelled event. As the UCWI changes during events, the model will tend to under-predict the runoff at the end of a storm, which is more marked for longer events; however this is not felt to be usually significant (Chapman, 1996). For the purposes of this study, the emphasis was on the first part of the runoff, so estimation of the recessional limb of the storm was not critical. Rainfall data from the two raingauges were employed in the modelling simulations.

For all storm simulations, baseflow was modelled as infiltration from the rural catchment, by taking Starflow measured discharge at the rural-urban juncture in $l\ s^{-1}$ and converting it to $m^3\ s^{-1}\ km^{-2}$. Soil moisture deficit (SMD) values, for the MORECS grid encompassing the site, were monthly long-term average values for the period 1961 - 1990, as current MORECS data was prohibitively expensive.

To assist in verification of the model, a rectangular thin-plate weir designed to BS 3680 4A (British Standards Institute, 1981) was installed immediately upstream of the juncture between the rural and urban portions of the catchment (Plate 7.1).

Plate 7.1: Weir sited at the downstream-rural point of the catchment (approximate National Grid Reference SK 3397 9656).

Installation took place on the 26th March, 2004. Data was subsequently downloaded weekly until the 4th May, 2004. Data was similarly taken from the downstream site.

The maximum depth over the weir crest was 0.2 m. Therefore, all depth measurements used in subsequent discharge calculations in excess of 0.2 m were disregarded as unreliable. Remaining storm events for which reliable discharge data existed were recorded, and the corresponding rainfall data were modelled using Hydroworks. In conjunction with the Starflow data logger at the downstream end of the brook, discharge values were derived with which to compare modelled events.

Following simulation runs of the storms, discharge files were produced for the nodes corresponding to the weir and to the downstream end of the catchment. These were exported to Excel to compare with empirically derived discharges. The results are displayed graphically below. The limitations of the Constant PR Model can be seen with regard to the extended data set for the 4th and 5th of May (figure 7.1), where the increased catchment wetness did not translate to increased discharge. The less flashy response of the rural compared to the urban portion of the catchment was evident.

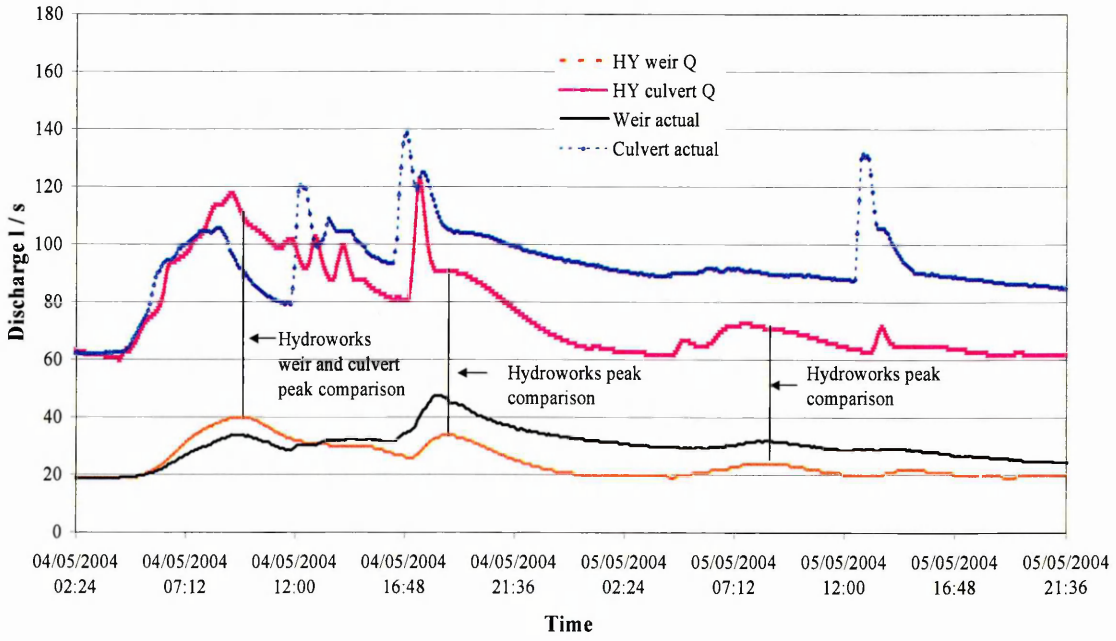


Figure 7.1: Extended Hydroworks simulation of the 4th and 5th of May, 2004.

Figures 7.2, 7.3 & 7.4 below, illustrate more detailed results for individual rainfall events with corresponding hyetographs.

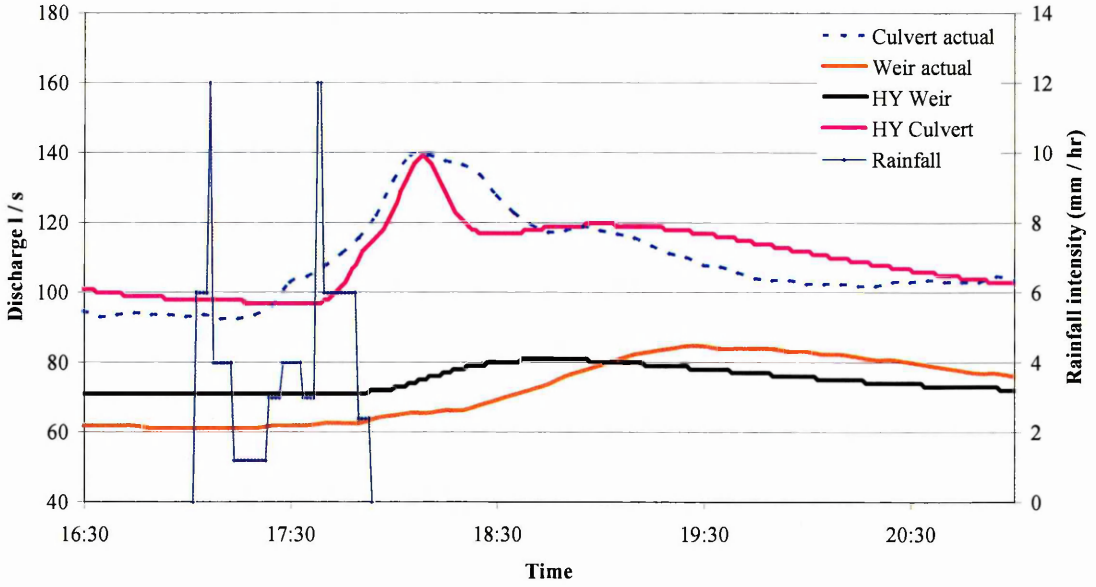


Figure 7.2: Modelled storm event of the 4th of April, 2004.

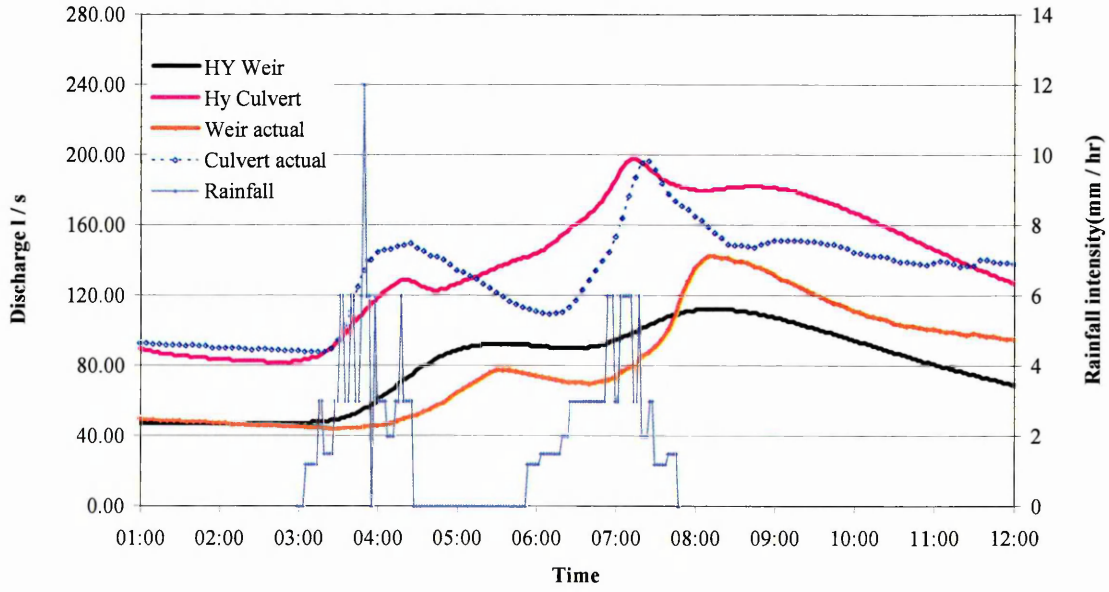


Figure 7.3: Modelled storm event of the 27th of April, 2004.

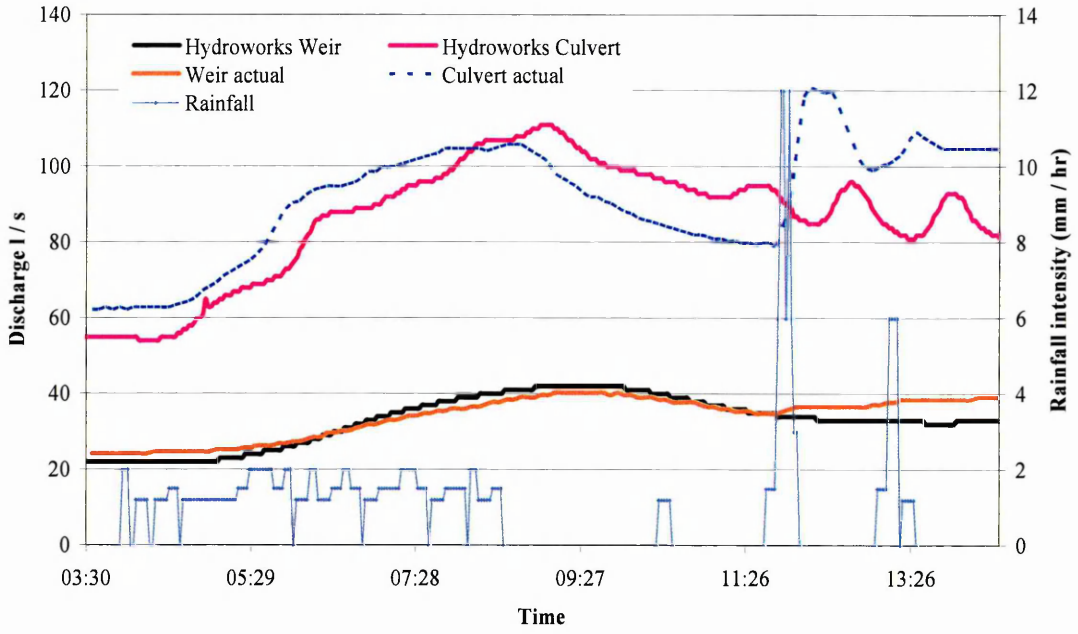


Figure 7.4: Modelled storm event of the 4th of May, 2004.

The utility of the model in predicting discharge at the weir can be seen in figure 7.5 below, which shows the modelled storm event of the 21st of July, 2003. One simulation of the event was produced by running the rainfall data through the model incorporating both permeable and impermeable surfaces, to represent the actual catchment. A second simulation was likewise produced by running the data through the same model but with all surfaces modelled as permeable to simulate a rural-only catchment. The derived 'rural' discharge was subtracted from the total. The resulting net discharge, clearly demonstrated that the sampled pollutants were associated with the urban runoff.

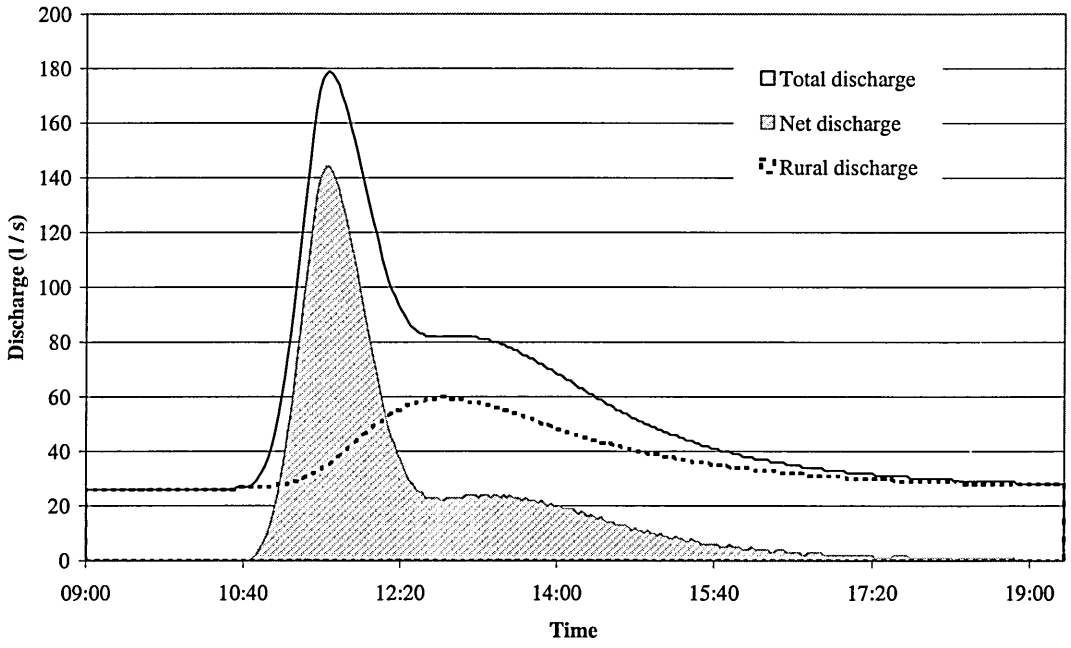


Figure 7.5: Graph of modelled storm event of the 21st of July 2003, showing the discharge associated with urban runoff.

7.3 Storm sampling

Sampling frequency was dependent on the system response time during any given storm event, commencing before the stream began to respond to the rainfall and maintained for as long as practicable on the recessional limb of the storm. All samples were taken by hand using 2 - litre polyethylene containers in midstream. Cognisance was taken by the author of the need to sample alone. Therefore sampling took place at site g, which represents the point below all discharges to the watercourse. In total, ten storms were successfully sampled for biochemical parameters and seven for trace metals. Figures 7.6 & 7.7 show the biochemical results from two of the sampled storms in association with measured discharge.

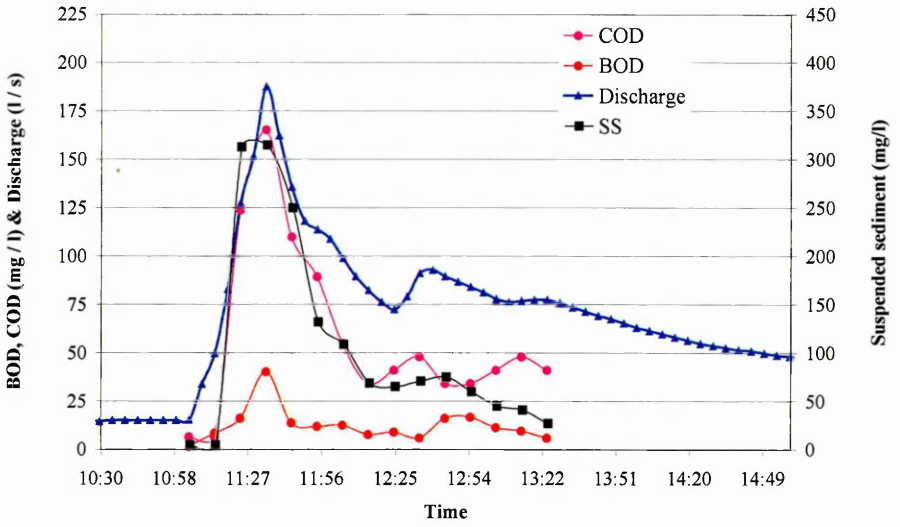


Figure 7.6: Graph of storm biochemical results for the 21st of July, 2003.

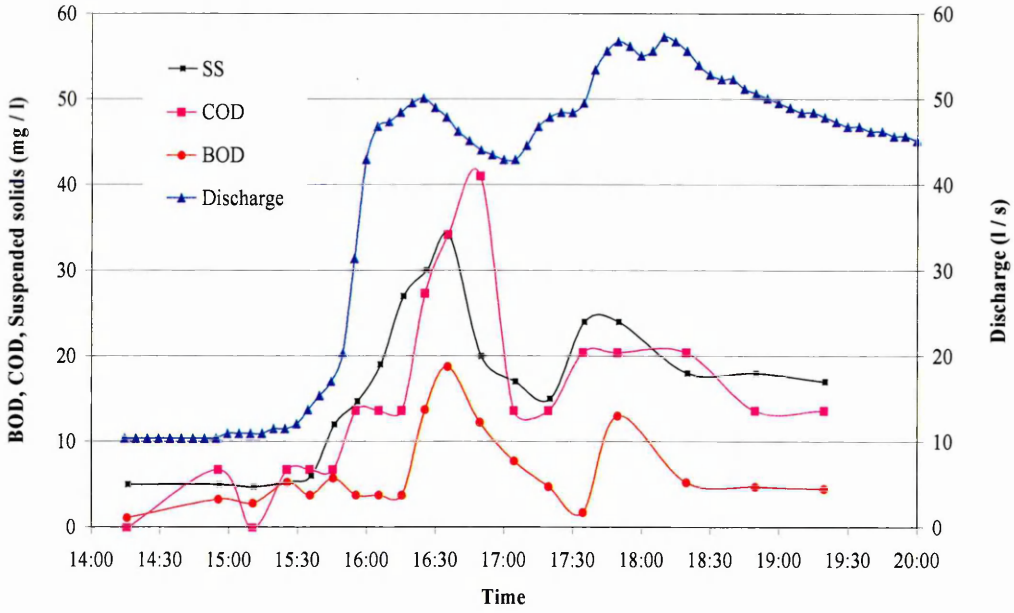


Figure 7.7: Graph of storm biochemical results for 29th of July, 2003.

Average dry-weather flow concentrations of the biochemical parameters were compared to the peak storm pollutant concentrations. As expected, all parameters with the exception of DO, increased. Generally, peak concentrations increased by an order of magnitude, notably with BOD and suspended sediment concentrations.

Results for ammonia, BOD, COD, and suspended solids were also less than the reported median EMC values reported in the NURP study for residential areas (U.S.EPA, 1983). The COD : BOD ratio (discussed in Chapter Five) was much reduced, as a consequence of the increased storm BOD concentration. Water quality parameters exhibit large variations throughout each runoff event. Some events exhibit the first flush effect, and in others the first flush effect has not been noticeable (Novotny & Olem, 1994). Therefore results from metals analysis and discharge data were used to produce event mean concentrations (EMC). EMC can be defined simply as the mass of pollutant from runoff event / total flow volume of event thus:

$$EMC = \frac{\int C(t)Q(t)dt}{\int Q(t)dt}$$

where;

C (t) and Q (t) are the time variable concentration and flow, measured during the runoff event.

It is clear that EMC results from a flow-weighted average, not simply a time-weighted average of the concentration. Statistical analysis of the storm biochemical EMCs confirmed a significant correlation between BOD & COD, BOD & suspended sediment and COD & suspended sediment ($p = 0.007$, 0.008 & 0.013 respectively). In all cases, mean storm concentrations conformed to the general range associated with surface water sewers detailed in table 7.1. Table 7.2 overleaf, shows the results of the storm biochemical analyses from Charlton brook.

	Surface water sewers	**Combined sewers**
Pollutant	Event mean concentrations ($mg\ l^{-1}$)	Event mean concentrations ($mg\ l^{-1}$)
Suspended solids	190 (21 - 2582)	425 (176 - 647)
BOD	11 (7 - 22)	90 (43 - 225)
COD	85 (20 - 365)	380 (250 - 530)
NH_4	1.45 (0.2 - 4.6)	6.0 (3.1 - 8.0)

Table 7.1: Example of the range of biochemical parameter concentrations observed from different sources of wastewater. Figures in parenthesis give range of observed mean values. Source: Ellis (1991).

Storm date (2003)	Ammonia (mg l^{-1})	BOD (mg l^{-1})	COD (mg l^{-1})	DO (mg l^{-1})	pH (mg l^{-1})	Suspended sediment (mg l^{-1})
January 17th	0.11	4.3	27.1	82.8	7.9	13.8
January 21st	1.55	9.0	35.2	83.8	8.0	72.4
March 4th	0.18	4.1	29.3	96.8	7.9	21.8
March 10th	0.06	3.0	53.2	93.8	7.9	30.4
April 1st	0.44	13.4	43.9	84.1	7.3	41.3
April 24th	0.85	23.6	107.7	74.6	7.9	113.1
June 27th	0.57	7.3	54.6	58.1	7.4	32.4
July 21st	0.26	15.3	73.3	70.9	7.9	136.4
July 29th	0.26	6.9	18.2	60.6	7.8	18.9

Table 7.2: Storm event mean concentrations of biochemical parameters; Charlton Brook.

Storm concentrations of metals

The results from the stormwater sampling campaign were compared with work completed by others (Maltby *et al.*, 1995a, 1995b; Makepeace *et al.*, 1995; Ellis & Revitt, 1982). Maltby *et al.*, (1995a) reported average concentrations of a number of metals in motorway runoff for three sites along the M1 motorway. The comparison of the highest averages over the three sites with Charlton Brook data is set out table 7.3 below. As can be seen from the table, Charlton Brook has experienced mean concentrations of aluminium, cadmium and chromium in excess of that determined by Maltby *et al.* (ibid). Copper, iron, nickel, lead and zinc were all reduced in comparison, although it should be noted that figures quoted from their study relate to the highest values obtained over three sites. Aluminium, cadmium and chromium levels for Charlton Brook exceed those for the MI motorway sites. However, this has been noted elsewhere by Ellis & Revitt (1982) who suggested that it may indicate possible heavy metal inputs from sources other than vehicles, citing work by Shaheen (1975), who showed concrete surfaces could yield high levels of lead and zinc in comparison to asphalt surfaces.

Comparison of stormwater metal concentrations (μg/L)					
Metal	Charlton Brook EMC (site *g*)	Maltby *et al.*, (1995) highest ave'	Makepeace *et al.*, (1995)	Makepeace *et al.*, (1995) Min & max means	Ellis (1982)
Ag	1.07	--	0.2 - 14	--	--
Al	886.34	131.5	100 - 16000	--	--
Be	2.40	--	1 - 49	--	--
Cd	5.19	<1	0.05 - 13730	0.3 - 11	0.8 - 8
Cr	19.87	4	1 - 2300	10 - 230	--
Cu	26.82	128.6	0.06 - 1410	6.5 - 150	7 - 1410
Fe	1759.48	3850	80 - 440000	988 - 12000	1000 - 85000
Hg	--	--	0.05 - 67	--	--
Mn	292.59	--	7 - 3800	110 - 670	7 - 3400
Na	--		180 - 660000	--	
Ni	7.14	15.5	1 - 49000	6 - 150	--
Pb	25.55	42.1	0.57 - 26000	20.9 - 1558	250 - 26000
Zn	47.02	489.1	0.7 - 22000	16.6 - 580	8 - 4600

Table 7.3: Comparison of stormwater metal concentrations from Charlton Brook with those published elsewhere in the literature.

Instream metal concentrations from storm events generally fell within the range reported by others. Figures 7.8 & 7.9 overleaf, illustrate the concentrations of metals during two of the sampled storm events.

Laboratory investigations into pulse exposure of cadmium on *Gammarus pulex* by Brooks *et al.* (1996) indicate that the way in which a dose is discharged, rather than the dose itself, is important in determining toxicity and hence, impact. Thus short, acute exposures may result in significantly lower survival rates than lower, constant concentrations over longer durations. Potentially, this highlights a weakness in traditional long duration exposure tests. Typically, these are run until a given percentage of the test organisms are dead, yet their lengthy duration may mask the lethal exposure 'required' to effect mortality, delivered in the initial stages of the test; a phenomenon suggested by McCahon & Pascoe (1990). Whilst Brent & Herricks (1998) showed that sufficient time in clean water following exposure to pulses of cadmium, zinc and phenol, allowed varying degrees of recovery in organisms; 'clean' water may not be a feature of natural systems exhibiting chronic low-level effects between pulses. Frequent exposure to such events may result in significant effects on the streams biota when coupled with chronic low level instream concentrations.

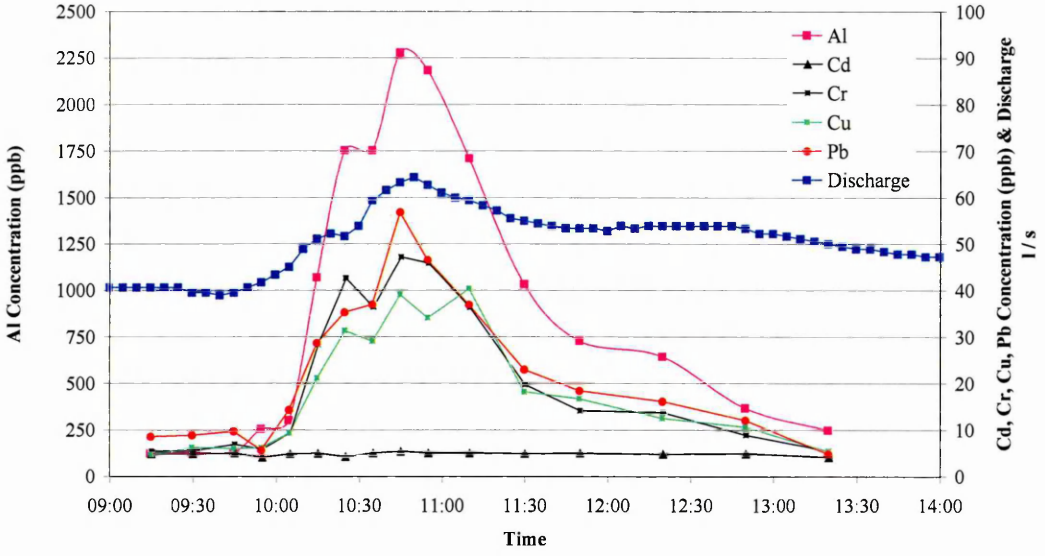


Figure 7.8: Metal concentrations for the storm of the 4th of March, 2003.

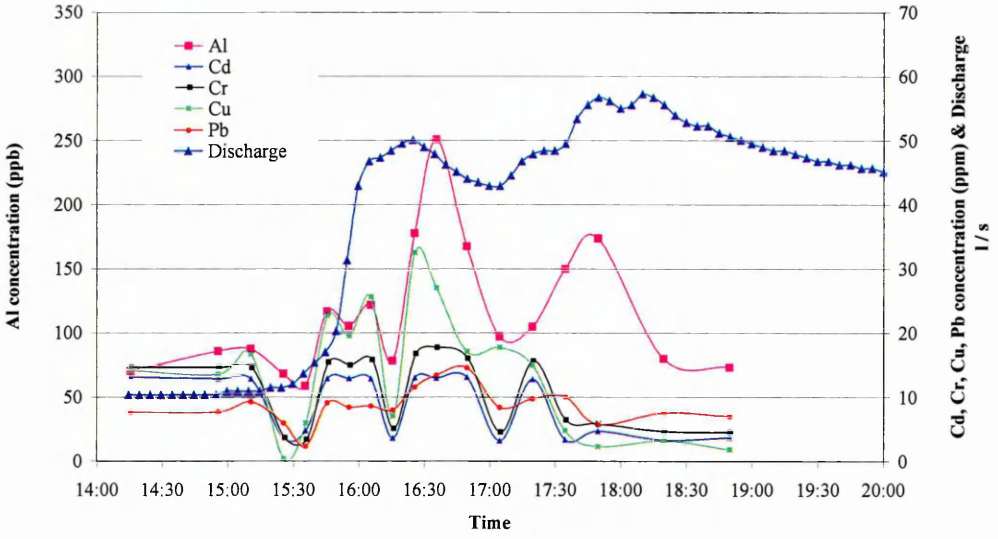


Figure 7.9: Metal concentrations for the storm of the 29th of July, 2003.

Copper, cited as the major aquatic toxic metal (Danneker *et al.*, 1990) exceeded the acute concentration set by the EPA, in 60 % of all samples taken during storms. Copper levels exceeded the one hour maximum concentration of 18.5 $\mu g\, l^{-1}$ set by the EPA on six out of the seven storms sampled for metals. As expected, lead levels

determined from storm samples were not indicated in relation to acute toxicity although it has been shown to be synergistically toxic when combined with Copper or Zinc (Hall & Anderson, 1988). Cadmium in stormwater is mostly associated with dissolved solids (Morrison *et al.*, 1984), and levels of Cd to date, from Charlton Brook are clearly indicated as a potential source of toxicity. Baseflow water quality (Chapter 5) from the summer samples exceeded the chronic concentration standard at all urbanised sites. Cadmium levels exceeded the one hour maximum concentration of 2.8 $\mu g\, l^{-1}$ set by the EPA on five out of the seven storms sampled for metals.

Studies into metal mobility indicate increased adsorption of Cd and Cu with rising pH, with Pb being the least mobile heavy metal especially under reducing or non-acidic conditions (Lazzari *et al.*, 2000). Nickel is relatively mobile and water soluble, being predominantly associated with suspended sediment and organic matter.

Zinc is similarly mobile and water soluble; mostly associated with dissolved solids (Morrisson *et al.*, 1984). Although not considered as much of a threat to aquatic life as copper or lead, it does bioaccumulate easily in plants and animals (Makepeace *et al.* 1995). Zinc levels determined from storms were not indicated in terms of acute effects, failing to ever reach the threshold determined by the EPA.

Analysis of the storm metal data showed that iron, aluminium and manganese were significantly correlated with the suspended sediment load ($P = < 0.05$) in all cases. Lead and nickel were similarly correlated in 80 % of storms and to a lesser extent, copper and zinc in 60 % of cases. Cadmium was not indicated in this respect, seeming to confirm its' association with dissolved solids (Morrison *et al.*, 1984).

Iron and aluminium were significantly correlated with chromium, copper, lead, manganese and zinc ($P = < 0.01$). A similarly significant relationship existed between chromium, copper, manganese, nickel and zinc ($P = < 0.01$). Iron and aluminium were the most strongly correlated metals ($P = < 0.01$). Cadmium was inversely correlated to all metals with the exception of nickel, possibly suggesting a shared source of contamination.

The apparent relationship between iron and several of the metals may be due to the fact that heavy metals are known to naturally adsorb to the surface of iron solids. As a corrosion product from vehicles and building materials, iron is often to be found in association with metals such as chromium and zinc. Figure 7.10 below, of the storm of 21st July 2003, illustrates the association of metals with suspended sediment. All the

metals peaked in tandem with the suspended sediment. The small second peak at 12.45 was accompanied by a commensurate increase in all metals.

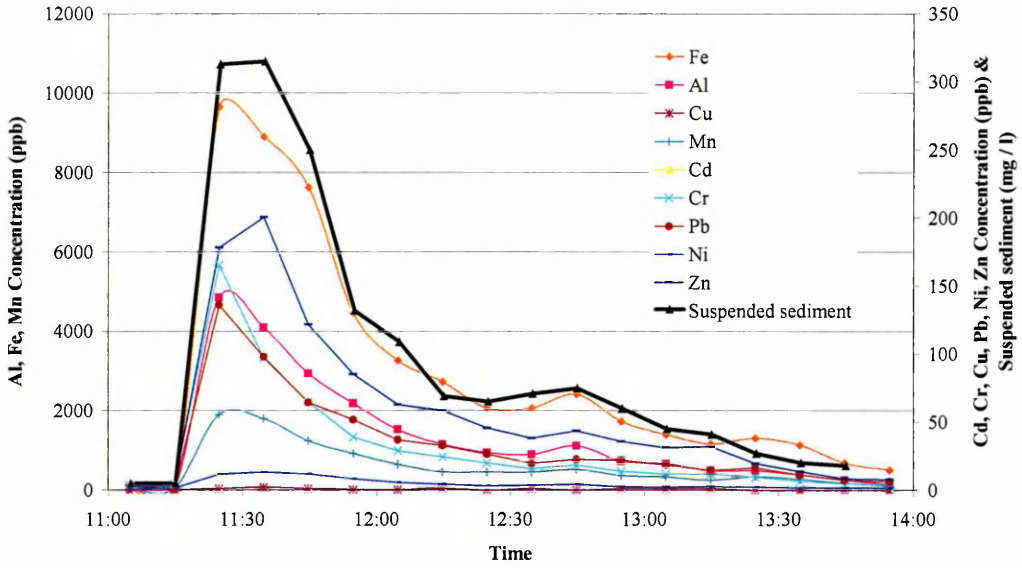


Figure 7.10: Association of all detected metals and suspended sediment for the storm of the 21st of July 2003.

Stormwater derived values would appear to suggest that copper, cadmium and aluminium were the main metals of concern from intermittent events within the catchment. A generally accepted method for accumulating the impact of pollutants during episodic events is not currently available. What could be determined, was the maximum concentration exceeded by any given metal over a one hour period from sampled storms in relation to the Criterion Maximum Concentration (CMC) values contained within the U.S. EPA guidelines, the assumption being that any value in excess of 1 indicated potential toxicity. Aluminium exceeded the EPA acute criteria on 4 occasions with cadmium and copper exceeding the threshold on 5 and 6 occasions respectively. It is probably no accident therefore, that in terms of generalised stormwater toxicity, cadmium and copper in particular are ranked the highest (Stormwater Industry Association, 2004). The reduced levels of lead from storm samples would seem to confirm that it is indeed becoming less of a problem now due to its virtual absence from fuel, though the higher levels in the water column seem to confirm its persistence within the sedimentary sink.

In terms of the total mass of metals determined from storm events, iron, aluminium and manganese were by far the most abundant, accounting for 95 % of the total (Fig 7.11).

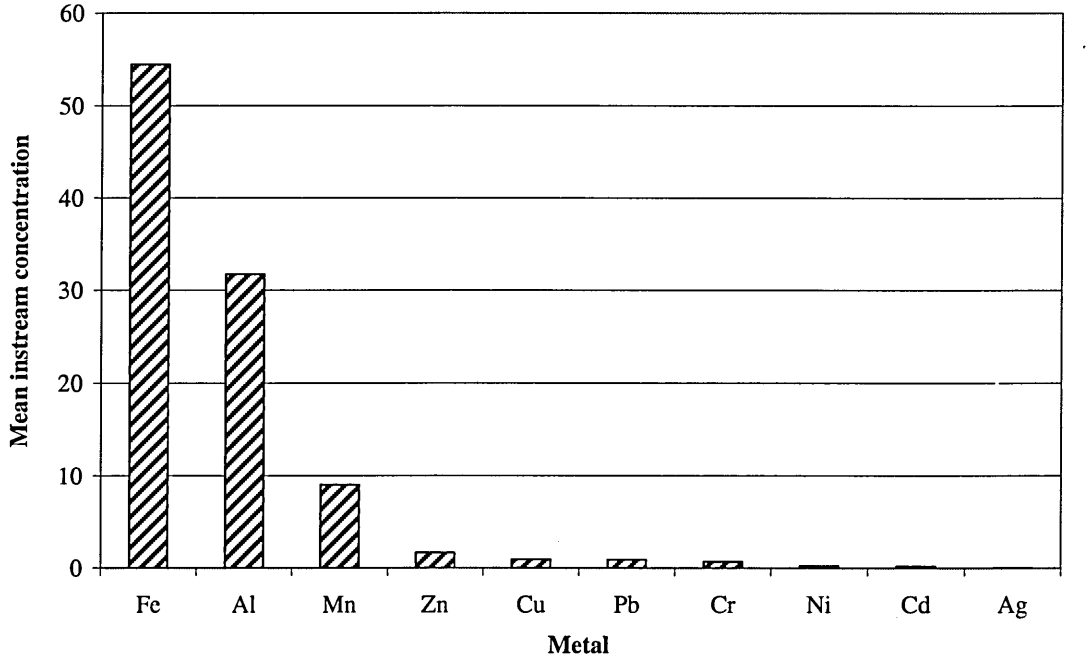


Figure 7.11: Mean percentage concentration of total instream metal during storm events.

Studies have shown that of the metals released from road and vehicle pollution, zinc is transported in the greatest quantity followed by copper and lead and, to a lesser extent, chromium and cadmium (Transport Research Laboratory, 2002). Iron and aluminium, which form a significant component of the total metal within the brook, have also been detected in significant amounts in other studies of road runoff. These were believed to be primarily products of corrosion and not toxic in the concentrations observed (Wilson, 1999). Manganese, which is also a constituent of steel used in vehicles, is implicated in affecting algal species at the base of food webs (Malmquist, 1978; cited in Novotny & Olem, 1994). All metals that were reliably determined, increased in concentration during storm events.

7.4 Summary

Stormwater discharges to watercourses can have numerous impacts, although their intermittent and unpredictable nature means that regular chemical sampling, typically practiced during low flows, often fails to detect high chemical and suspended sediment inputs. Hydrometric data reveal that the catchment experienced 430 separate rainfall events between March 2002 and January 2004; the period encompassing the GQA-based sampling; however, all these samples were obtained during dry-weather flow conditions.

Hydraulic modelling of the stormwater drainage network within the catchment using Hydroworks, demonstrated that polluted water associated with flow from SWOs. Low baseflows can result in little dilution of pollutants associated with SWOs within the brook.

All metal and biochemical determinants were elevated during storm events with concentrations similar to those reported in other studies.

At present, there is no commonly accepted method for evaluating the toxic impact of stormwater. Indeed, the response of macroinvertebrates to cocktails of pollutants within the laboratory has still to be fully defined.

In the absence of standards for the acute impact from stormwater discharges comparison of the sample data was made with the EPA acute criteria which has indicated that aluminium, cadmium and copper occur at potentially toxic concentrations during storm events.

Chapter 8

Conclusions and recommended further research

Conclusions

The objective of this study was to investigate the stream quality within a small urbanised catchment. This was successfully achieved through determination of the physico-chemical and biological characteristics of the watercourse, primarily guided by the work of established researchers such as the Biological Monitoring Working Party, Burton, Ellis, Mason and Wright. In addition, this study was augmented by integrating the results of other component investigations for sediments, PAHs and metals. The novel application of techniques described within the thesis indicates that the benthic macroinvertebrate population of the watercourse is adversely affected by stormwater inputs, with a marked drop in biological diversity occurring with the onset of urbanisation.

The upstream site (a) had the lowest sediment related levels of cadmium, chromium, copper, lead and zinc. However, the majority of individual metal concentrations did not vary significantly between the different urbanised sites. Only chromium at site d exceeded the stated threshold. Sediments were also analysed for PAHs, with all sites being impaired. Results suggested their primary source as originating from combusted fuels. Statistical analysis of mean PEL-quotient values and the impermeable areas associated with those surface water outfalls immediately upstream of sampling sites showed a significant correlation (0.892, $p = 0.042$), suggesting that sediment bound pollutants are in proportion to the impermeable areas from which they are generated whilst remaining fairly localised within the stream bed. The highest levels of pollution occurred at the onset of urbanisation and at the furthest downstream sampling point.

Physico-chemical grading of the brook illustrated a decline in quality between the rural and downstream urban site. BOD and DO results indicated a greater drop in quality over the length of the watercourse than that suggested by ammonia. Elevated levels of this determinand within the rural portion of the catchment are possibly attributable to agricultural application of slurry.

Levels of chronic pollution by dissolved metals were determined by CCU scores. This illustrated significant temporal differences between seasons, suggesting

potential chronic toxicity at all sites, particularly within the urbanised portion of the catchment. *Prima facie* evidence suggests that both CCUs and mean PEL-quotients may be beneficial in determining whether the potential for toxicity exists. The biological indices support this view. However, with the exception of stoneflies, there was a lack of correlation between macroinvertebrates and individual pollutants and / or the cumulative measures of toxicity employed. Significantly, diversity correlated with cumulative impermeable area, although the reasons for this in relation to multiple stormwater inputs demand further investigation.

Biological GQA of the brook placed it in a lower grade than that derived from the chemical grading. The biology at the downstream urban site was significantly poorer than that of the rural. The biotic ASPT and BMWP scores encapsulate the observed trend of a decreasing abundance of sensitive families with increasing abundance of pollution tolerant families such as *Asellidae*, suggesting the presence of organic pollution, a well documented constituent of stormwater runoff (Hvitved-Jacobsen, 1986; House *et al.*, 1993). The increased abundance of *Asellidae* in the urban portion of the catchment was accompanied by an equivalent decline in *Gammaridae* (freshwater shrimps), possibly reflecting the greater sensitivity of gammarids to ammonia and other effluents (Mullis *et al.*, 1996). However, this overall trend of reduced species richness, and a shift from sensitive to tolerant taxa may also be an indication of metal pollution (Clements, 1994), with the decline in number of taxa seen as a general indicator of overall pollution which includes organic and toxic pollution (E.A., 2003). Calculated diversity indices, which were typical of a stressed environment within the urbanised part of the catchment, support this. Both the Shannon-Weiner and Simpson indices for the Autumn samples, correlated significantly with cumulative impermeable area, both suggesting that an increase in impermeable area equates to a reduction in diversity. Neither of these indices from the Spring sampling correlated significantly with increasing impermeable area however. In contrast, the BMWP scores were inversely correlated with cumulative area in the Spring, but not in the Autumn.

EPT abundance was significantly correlated to sediment copper and lead. However, there was no replacement of sensitive mayfly taxa by metal-tolerant species of caddis such as *Hydropsychidae*, as has been reported elsewhere (Clements & Kiffney, 1994). EPT abundance demonstrated a significant inverse correlation with the

impermeable areas associated with each sampling site, both in Spring and Autumn. When considered in tandem with the relationship between PEL and area, there appears to be the suggestion that the admixtures of pollutants contained within the sediment have a bearing on the diversity of the brooks' macroinvertebrate assemblage.

Instream concentrations of cadmium and lead showed a significant negative correlation with all the stonefly families, *Heptagenid* mayflies and the *Polycentropidae* and *Rhyacophilidae* caddis families. Diptera numbers increased significantly at the upstream site between the spring and autumn, rising from 4 % to 20 % of total assemblage, yet within the urbanised sites simulidae and tipulidae were all but absent. Diptera larvae are particularly sensitive to trace metals (Shutes, 1984) and their reduced abundance within the brook possibly reflected the rise in instream metal concentration.

The concentrations of sampled storm parameters were compared to chronic levels within the brook. All biochemical parameters with the exception of dissolved oxygen increased, with peak concentrations an order of magnitude greater. Concentrations of BOD and COD showed a significant correlation to suspended sediment. In all cases, mean storm concentrations conformed to the ranges reported elsewhere for surface water sewers. Similarly, all sampled metals increased in concentration during storm events. Results for determined metals indicated that the brook had experienced mean concentrations of aluminium, cadmium and chromium in excess of that recorded for motorway runoff. Aluminium, cadmium and copper were particularly indicated during storm events, being those most commonly in excess of the acute threshold set by the EPA.

Preliminary hydraulic modelling of the stormwater drainage network within the catchment, has demonstrated that polluted water is associated with discharges from SWOs. Low baseflows effectively mean that there can be little dilution of pollutants associated with SWOs within the brook.

Benthic macroinvertebrate analysis has demonstrated a marked decline in biological integrity with the onset of urbanisation. A further deterioration occurs over the length of the urban watercourse. The poor biology of this unclassified river is attributable to pollutants from SWOs.

There is a paucity of research concerning urban watercourses within the UK, particularly those that receive inputs solely from surface water outfalls. The novel approach contained within this thesis suggests that these small catchments may suffer impacts commensurate with those typically associated with point-source discharges to classified watercourses. Future emphasis on water quality will hopefully encompass all sizes of water bodies, and it is hoped that this work will provide a valuable key reference for those wishing to understand the likely impacts associated with small urbanised catchments.

Recommendations for further research

Analysis has shown the potential for toxicity from stormwater discharges to the study watercourse. Specific facets, such as the amount of BOD associated with both baseflow and storms can be determined relatively easily. However, a great deal of further thought is needed before evaluation of the risk of all forms of both chronic and acute pollution to aquatic life is possible. For example, there are numerous disparate standards for many, but not all of the pollutants discussed in this study. Additionally, the recovery of macroinvertebrates below discharges is currently poorly defined in terms of distance.

References

Abel, P. D. (1980). A new method for assessing the lethal impact of short-term, high-level discharges of pollutants on aquatic animals. *Progress in Water Technology*, **13**, 347-352.

Abel, P. D. & Gardner, S. M. (1986). Comparisons of Median Survival Times and Median Lethal Exposure Times for Gammarus Pulex exposed to Cadmium, Permethrin and Cyanide. *Water Research,* **20**(5), 579-582.

Abesser, C. & Soulsby, C. (2002). Sources of Iron and Manganese in Public Water Supplies: A Case Study of the Megget Reservoir, Scotland. *Fourth International Conference on Reservoir Limnology and Water Quality, Ceske Budejovice*, Icarus Ltd, Prague, 29-32.

Alloway, B. J. & Ayres, D. C. (1997). *Chemical Principles of Environmental Pollution*, 2nd edn, Chapman & Hall, London.

Apitz, S. E., Burt, N., Cook, S. R., Fletcher, C., Murray, L., Parker, A., Power, E. A., Wilkinson, H., & Wright, T. (2003). Holistic Sediment Management: UK Goals, Needs and Approaches - Workshop Report, University of Reading.

Armitage, P. D. (1980). The effects of mine drainage and organic enrichment on benthos in the River Nent System, Northern Pennines, *Hydrobiologia*, **74**, 119-128.

APHA. (1998). Standard Methods 20th Edition, American Waterworks Association.

Ball, J. E., Jenks, R., & Aubourg, D. (1998), An Assessment of the Availability of Pollutant Constituents on Road surfaces. *The Science of the Total Environment*, **209**, 243-254.

Barbour, M. T., Gerritson, J., Griffith, G. E., Frydenborg, R., McCarron, E., White, J. S., & Bastian, M. L. (1996). A framework for biological criteria for Florida streams using benthic macroinvertebrates. *Journal of the North American Benthological Society*, **15**(2), 185-211.

Beasley, G. & Kneale, P. (2002). Reviewing the impact of metals and PAHs on macroinvertebrates in urban watercourses. *Progress in Physical Geography*, **26**(2), 236-270.

Beasley, G. & Kneale, P. (2003), Investigating the influence of heavy metals on macroinvertebrate assemblages using Partial Canonical Correspondence Analysis (pCCA). *Hydrology and Earth System Sciences*, **7**(2), 221-233.

Beech, L. (2001). Biomonitoring of the River Almond - The Effects of Organic Enrichment on Water Quality and Macro-Invertebrate Communities. Unpublished MSc. dissertation, Napier University, Edingburgh.

Bender, G. M. & Terstrep, M. L. (1984). Effectiveness of Street Sweeping in Urban Runoff Pollution Control. *The Science of the Total Environment*, **33**, 185-192.
Bertrand-Krajewski, J., Chebbo, G., & Saget, A. 1998, Distribution of Pollutant Mass Vs Volume in Stormwater Discharges and the First Flush Phenomenon. *Water Resources,* **32**(8), 2341-2356.

Biological Monitoring Working Party. (1978). *Final Report: Assessment and Presentation of Biological Quality of Rivers in Great Britain.* Unpublished Report, Department of the Environment, Water Data Unit.

Boxall, A. B. A. & Maltby, L. (1997). The effects of motorway runoff on freshwater ecosystems: 3. Toxicant confirmation. *Arch. Environmental Contamination and Toxicology*, **33**, 9-16.

Bradford, W. L. (1977). Urban Stormwater Pollutant Loadings: A Statistical Summary Through 1972. *Journal of the Water Pollution Control Federation*, **49**, 613-622.

Brent, R. N. & Herricks, E. E. (1998). Postexposure effects of brief cadmium, zinc and phenol exposures on freshwater organisms. *Environmental Toxicology and Chemistry,* **17**, 2091-2099.

Brick, C. M. & Moore, J. N. (1996). Diel Variation of Trace Metals in the Upper Clark fork River, Montana, *Environmental Science and Technology*, **30**,1953-1960.

Brinkmann, W. L. F. (1985). Urban Stormwater Pollutants: Sources and Loadings. *GeoJournal,* **11**(3), 277-283.

British Standards Institute. (1981). *BS 3680-4A: Measurement of liquid flow in open channels - Part 4A: Method using thin-plate weirs.* London, British Standards Publications Limited.

Brooks, A. W., Maltby, L., Saul, A. J., & Calow, P. (1996). A Simple Indoor Artificial Stream System Designed To Study The Effects Of Toxicant Pulses On Aquatic Organisms. *Water Research*, **30**(2), 285-290.

Brown, B. E. (1976). Observations on the tolerance of the isopod *Asellus meridianus* Rac. to copper and lead. *Water Research*, **10**, 555-559.

Buhs, J. (2000). Making Humic Substances More Biodegradable. Montana State University. www.evc.montana.edu/Res-Lib99-SW/PubsTheses/2000/Thesis00_Buhs.htm. 31-10-01.

Burton, G. A., Pitt, R. & Clark, S. (2000). The Role of Traditional and Novel Toxicity Test Methods in Assessing Stormwater and Sediment Contamination. *Critical Reviews in Environmental Science and Technology*, **00**(0), 1-35.

Burton, G. A. & Pitt, R. E. (2002). *Stormwater Effects Handbook: A Toolbox for Watershed Managers, Scientists, and Engineers.* Lewis Publishers, London.

Butler, D. & Davies, J. W. (2000). *Urban Drainage.* 1st edn, E & FN Spon, London.

Canadian Council of Ministers of the Environment. (1995). *Protocol for the Derivation of Canadian Sediment Quality Guidelines for the Protection of Aquatic Life.* Environment Canada, Ottawa, CCME EPC-98E.

Canadian Council of Ministers of the Environment. (1998). *Canadian Sediment Quality Guidelines for the Protection of Aquatic Life.* Prepared by Environment Canada, Guidelines Division, Ottawa, CCME EPC-98E.

Canadian Council of Ministers of the Environment. (2001). *Canadian Sediment Quality Guidelines for the Protection of Aquatic Life: Summary Tables.* Manitoba Statutory Publications, Winnipeg.

Carleton, M. G. (1990). Comparison of Overflows From Separate and Combined Sewers. Quantity and Quality. *Water Science and Technology*, **22**(10-11), 31-38.

Cessford, F. (1997). *A Report Investigating Observed Discrepencies Between Biological and Chemical Classifications on Blackburn Brook, Sheffield.* Environment Agency, North East Region Ridings Area, 390 DON4.

Chapman, R. E. (1996). *The Percentage Runoff Equation.* WaPUG User Note No 9. Water Research Centre, Swindon.

Chocat, B., Krebs, P., Marsalek, J., Rauch, W., & Schilling, W. (2001). Urban Drainage Redefined: From Stormwater Removal to Integrated Management. Water Science and Technology, **43**(5), 61-68.

Christenson, J. S. & Elton, J. (1996). Soil and Groundwater Pollution From BTEX. *Groundwater Pollution Primer.* Civil Engineering Department Virginia Tech.

CIES. Sensitivities of BMWP taxa to chemical and environmental factors. (2002). Centre for Intelligent Environmental Systems, Staffordshire University.

Clarke, R. T., Wright, J. F., & Furse, M. T. 2003. RIVPACS models for predicting the expected macroinvertebrate fauna and assessing the ecological quality of rivers, *Ecological Modelling*, **160**, 219-233.

Clements, W. H. (1994), Benthic Invertebrate Community Responses to Heavy Metals in the Upper Arkansas River Basin, Colorado. *Journal of the North American Benthological Society*, **13**(1), 30-44.

Clements, W. H. & Kiffney, P. M. (1994). Integrated laboratory and field approaches for assessing impacts of heavy metals at the Arkansas River, Colorado. *Environmental Toxicology and Chemistry*, **13**, 397-404.

Clements, W. H., Carlisle, D. M., Lazorchak, J. M., & Johnson, P. C. (2000). Heavy metals structure benthic communities in Colorado mountain streams, *Ecological Applications*, **10**, 626-638.

Coimbra, C. N., Graca, M. A. S., & Cortes, R. M. (1996). The Effects of a Basic Effluent on Macroinvertebrate Community Structure in a Temporary Mediterranean River. *Environmental Pollution*, **94**(3), 301-307.

Cole, S., Whitehouse, P., Harrison, R., Holmes, D., Zabel, T., Johnson, I., Sorokin, N., Adeboya, T., Crane, M., Matthiessen, P., & Dubourg, R. (2003). *Derivation of Aquatic Quality Standards for priority List Substances not Covered by Existing UK Regulations. Final Report to the Department for Environment, Food and Rural Affairs*. DEFRA, 6245/2.

Coomhola Salmon Trust. (2001). Streamscapes. http://www.streamscapes.org/ . 12/02/2003

Croft, P. S. (1986). *A Key to the Major Groups of British Freshwater Invertebrates.* Field Studies Council & AIDGAP, Preston Montford.

Crunkilton, R., Kleist, J., Ramcheck, J., DeVita, B., & Villeneuve, D. (1996). Assessment of the response to aquatic organisms to long term *in situ* exposures to urban runoff. In: *Effects of Watershed Development and Management on Aquatic Ecosystems, Engineering Foundation Conference*: Snowbird, Utah, ASCE, New York.

CSMWG. (2003). A Method for Ranking Contaminated Aquatic Sites on Canadian Federal Properties (Final Version). http://www.ec.gc.ca/etad/csmwg/pub/marine_aquatic/en/chap3_e.htm . Government of Canada. 6-6-2004.

Cubbage, J., Batts, D., & Breidenbach, S. (1997). *Creation and Analysis of Freshwater Sediment Quality Values in Washington State*. Washington State Department of Ecology, Olympia, WA., 97-323a.

Dahle, S., Savinov, V. M., Maishov, G. G., Evenset, A., & Næs, K. (2003,). Polycyclic aromatic hydrocarbons (PAHs) in bottom sediments of the Kara Sea shelf, Gulf of Ob and Yenisei Bay. *The Science of the Total Environment*, **306**, 57-71.

Dannecker,W., Au, M. & Stechmann,H. (1990). Substance load in rainwater runoff from different streets in Hamburg. *The Science of the Total Environment*, **93**, 385.

Davis, G. & Ghabbour, E. About Humic Substances. Northeastern University . 2001. 31-10-0001.

Davis, J. B. & George, J. J. (1987). Benthic invertebrates as indicators of urban and motorway discharges. *Science of the Total Environment*, **59**, 291-302.

Dawson, S. Pathogens Within Other Waste Water Flows. Canoeists Pathogenic Illness Guide. (2001). 1-11-0001.

DEFRA. (2004). e-Digest Statistics about: Air Quality. http://www.defra.gov.uk/environment/statistics/airqual/aqmetals.htm#aqtb25 . 07/04/2004.

Deletic, A. (1998). The First Flush Load of Urban Surface Runoff. *Water Research,* **32**(8), 2462-2470.

Desbordes, M. & Hemain, J. C. (1990). Further research Needs for Impact Estimates of Urban Storm Water Pollution. *Water Science and Technology,* **22**(10-11), 9-14.

DETR. (2001). *First Consultation Paper on the Implementation of the EC Water Framework Directive.* Department of the Environment Transport and regions.

Edington, J. M. & Hildrew, A. G. (1995). *A Revised Key to the Caseless Caddis Larvae of the British Isles, with notes on their ecology.* Freshwater Biological Association, Ambleside.

Edwards, R. W., Ormerod, S. J., & Turner, C. (1991). Field experiments to assess biological effects of pollution episodes in streams. *Verhandlungen Der Internationalen Vereinigung Fur Theoretische Und Angewandte Limnologie*, **24**, 1734-1737.

Elliot, J. M., Humpesch, U. H. & Macan, T. T. (1988). *Larvae of the British Ephemeroptera: a key with ecological notes.* Freshwater Biological Association, Ambleside.

Ellis, J. B. (1979). The Nature and Sources of Urban Sediments and Their Relation to Water Quality. In: *Man's Impact on the Hydrological Cycle in the United Kingdom*, 1st edn, G. E. Hollis, (ed),199-216.

Ellis, J. B. (1986). Pollutional Aspects of Urban Runoff. In *Urban Runoff Pollution*, H. C. Torno, J. Marsalek, & M. Desbordes, (eds), Springer-Verlag, New York.

Ellis, J. B. (1989). *Urban Discharges and Receiving Water Quality Impacts.* 1st edn, Pergamon Press, Oxford.

Ellis, J. B. (1991. Urban Runoff Quality in the UK: Problems, Prospects and Procedures. *Applied Geography*, **11**(3), 187-200.

Ellis, J. B. & Hvitved-Jacobsen, T. (1996). Urban Drainage Impacts on Receiving waters. *Journal of Hydraulic Research,* **34**(6), 771-783.

Ellis, J. B. & Revitt, M. (1982). Incidence of Heavy Metals Street Surface Sediments: Solubility and Grain Size Studies. *Water, Air and Soil Pollution*, **17**, 87-100.

English Nature (2001). *First consultation on the implementation of the EC Water Framework Directive: Response to DETR Consultation.*

Enserink, E. L., Maas-Diepeveen, J. L., & Van Leeuwen, C. J. (1991). Combined effects of metals; an ecotoxicological evaluation. *Water Research,* **25**(6), 679-687.

Environment Agency. 1997, Environment Agency Programme For The Monitoring Of Water Quality. Part 2: Design of Monitoring Programmes for General Quality Assessments. Environmental Monitoring Programme, Internal Document. 57-72.

Environment Agency (1998). *The State of the Environment of England and Wales: Fresh Waters.* HMSO, London.

Environment Agency. (2001). *General Quality Assessment of Rivers: Chemistry.* Environment Agency, Bristol.

Environment Agency (2002). *The Water Framework Directive: Guiding principles on the technical requirements.* Environment Agency, Bristol.

Environment Agency (2002b). *River Quality - an overview*, http://www.environment-agency.gov.uk/yourenv/eff/water/213902/river_qual/?lang=_e

Environment Agency (2003). *General Quality Assessment of Rivers: Biology.* Environment Agency, Bristol.

Environment Canada. Factsheet 2: *Chemical-Specific Sediment Quality Guidelines.* http://www.ec.gc.ca/ceqg-rcqe/English/Html/SAS/factsheet_2.cfm . (2004). Environment Canada. 29-3-0004.

European Council. (1975). Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water in the member states, L 194/26.

European Council. (1976,). Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the community.

European Council. (1991). Directive 91/271/EEC Urban Waste Water treatment. OJ No L 135/40.

European Council. (2000). Directive 2000/60/EC. Establishing a Framework for Community Action in the Field of Water Policy.

Faulkner, H., Edmonds-Brown, V., & Green, A. (2000). Problems of Quality designation in Diffusely Polluted Urban Streams - The Case of Pymme's Brook. *Environmental Pollution,* **109**, 91-107.

Field, R. & Pitt, R. (1990). Urban Storm-Induced Discharge Impacts: US Environmental Protection Agency Research Programme Review. *Water Science and Technology,* **22**(10-11), 1-7.

Field, R. & Turkeltaub, R. (1980). Don't Underestimate Urban Runoff Problems. *Water and Wastes Engineering*, October 1980, 48-52.

Field, R. & Turkeltaub, R. (1981). Urban Runoff Receiving Water Impacts - Programme Overview. *Journal of Environmental Engineering Division*, **107** (EE1), 83-100.

Fitter, R. & Manuel, R. (1995). *Lakes, Rivers, Streams and Ponds of Britain and North West Europe.* Harper-Collins, London.

Forster, J. (1996). Patterns of Roof Runoff Contamination and their Potential Implications on Practice and Regulation of Treatment and Local Infiltration. *Water*

Science and Technology, **33**(6), 39-48.

Forth River Purification Board, (1994). *Urban Surface Water runoff - Discharge Quality, Impact and Extent of the Problem in the Forth RPB.*

Furse, M. T. (1998). *The Faunal Richness of Headwater Streams*, Unpublished PhD thesis, University of Reading, Reading.

Furse, M. T. (2000). *The application of RIVPACS procedures in headwater streams - an extensive and important national resource.* In: *Assessing the biological quality of fresh waters. RIVPACS and other techniques*, J. F. Wright, D. W. Sutcliffe, & M. T. Furse, (eds), Freshwater Biological Association, Ambleside, 79-91.

FWR. (1997). National Consent Translation Project: Chemical Oxygen Demand of Sewage Effluents ('Hard COD') Final Report, http://www.fwr.org/wastedis/frcl0006.htm, 10/04/2002.

FWR. (1998). *Urban Pollution Management Manual.* Foundation for Water Research, FR/CL009. Marlow, Buckinghamshire.

Garnaud, S., Mouchel, J., Chebbo, G., & Thevenot, D. R. (1999). Heavy Metal Concentrations in Dry and Wet Atmospheric Deposits in Paris District: Comparison With Urban Runoff. *The Science of the Total Environment*, **235**(1-3), 235-245.

Gillis, C. A., Bonnevie, N. L., Hu, S. H., Ducey, G., Huntley, S. L., & Wenning, R. J. (1995). DDT, DDD, and DDE contamination of sediment in the Newark Bay Estuary, New Jersey. *Archives of Environmental Contamination and Toxicology*, **28**, 85-92.

Gray, J.S., McIntyre, A.D., & Stirn, J. (1992). Manual of methods in aquatic environment research. Part 11. Biological assessment of marine pollution with particular reference to benthos, FAO Fisheries Technical Paper 324: 49 pp.

Green, A. & Faulkner, H. (2000). An Assessment of the Suitability of the Environment Agency's Water-Quality Classification System for Use in Urban Catchments, *Journal of the Chartered Institution of Water and Environmental Management*, **14**. 131-139.

Griffith, M. B., Barrows, E. M., & Perry, S. A. (1998). Lateral dispersal of adult aquatic insects (Plecoptera, Trichoptera) following emergence from headwater streams in forested Appalachian catchments. *Annals of the Entomological Society of America*, **91**, 95-101.

Gromaire, M. C., Garnaud, S., Ahyerre, M., & Chebbo, G. (2000). The Quality of Street Cleaning Waters: Comparison With Dry and Wet Weather Flows in a Parisian Combined Sewer System. *Urban Water*, **2**, 39-46.

Grottker, M. (1987). Runoff Quality From a Street With medium Traffic Loading. *The Science of the Total Environment*, **59**, 457-466.

Hall, K. J. & Anderson, B. C. (1988). The toxicity and chemical composition of urban stormwater runoff. *Canadian Journal of Civil Engineering*, **15**(1), 98-

Hall, K. (1997). *Impact of Stormwater Runoff on Urban Streams: A Case Study in the Brunette River Watershed.* In: *Workshop Proceedings: Urban Stream Protection, Restoration and Stewardship in the Pacific Northwest: Are We Acheiving Desired Results?* Douglas College, New Westminster, British Columbia, 10th March, 1997.

Hall, M. J. & Ellis, J. B. (1985). Water Quality Problems in Urban Areas. *GeoJournal*, **11**(3), 265-275.

Hall, M. J., Hockin, D. L., & Ellis, J. B. (1993). *Design of Flood Storage reservoirs.* 1st edn, CIRIA & Butterworth-Heinemann Ltd, Oxford.

Harremöes, P., Napstjert, L., Rye, C., Larson, H. O., & Dahl, A. (1996). Impact of Rain Runoff on Oxygen in an Urban River. *Water Science and Technology*, **34**(12), 41-48.

Harrop, D. O. (1984). *Stormwater Runoff and Water Quality in Urban Catchments*, PhD, Middlesex Polytechnic, Enfield.

Hawkes, H. A. (1979). *Invertebrates as indicators of water quality.* In: *Biological Indicators of Water Quality*, James, A. & Evison, L., eds., John Wiley & Sons, Chichester.

Heaney, J. & Huber, W. C. (1984). Nationwide Assessment of Urban Runoff Impact on Receiving Water Quality. *Water Resources Bulletin*, **20**(1), 35-42.

Heinonen, J. (2001). *Multiple Stress in Pisidium Amnicum (Bivalva) - Interactions of toxic chemicals, seasonal temperatures and trematode parasites.* Unpublished PhD thesis, University of Joensuu, Finland.

Henry, J. G. & Heinke, G. W. (1989). *Environmental Science and Engineerin.* Prentice Hall, New Jersey.

Herricks, E. E. & Jenkins, J. R. (1995). *Stormwater Runoff and Receiving Systems Impact Monitoring and Assessment.* Lewis Publishers, London.

Hirst, H., Juttner, I., & Ormerod, S. J. (2002). Comparing the responses of diatoms and macroinvertebrates to metals in upland streams of Wales and Cornwall. *Freshwater Biology*, **47**, 1752-1765.

Hoffman, E. J. 1984, Urban runoff as a source of polycyclic aromatics to coastal waters. *Environmental Science and Technology*, **18**, 580-587.

House, M. A., Ellis, J. B., Herricks, E. E., Hvitveld-Jacobsen, T., Seager, J., Lijklema, L., Aalderink, R. H., & Clifforde, I. (1993). Urban Drainage - Impacts on Receiving Water Quality. *Water Science and Technology*, **27**(12), 117-158.

Housebuilders Federation. *Building a Crisis - Britain's Housing Shortage.* http://www.hbf.co.uk/main.asp . (2002). 3-7-0002.

Huber, W. C. (1986). *Modelling Urban Runoff Quality: State of the Art.* In: *Modelling Runoff Quality*, H. C. Torno, J. Marsalek, & M. Desbordes, eds., Springer-Verlag, Heidelberg.

Hutchison Port UK Ltd. (2003. *Felixstowe South Reconfiguratio. Chapter Nine: Sediments*. http://www.portoffelixstowe.co.uk/. 14-11-2003.

Hvitved-Jacobsen, T. & Harremoes, P. (1982). *Impact of CSOs on the DO in receiving streams*. In: *Urban Stormwater Quality Management and Planning*, B. C. Yen, (ed). Water Resources Publications, Littleton, Colorado, 226-235.

Hvitved-Jacobsen, T. (1986). *Conventional Pollutant Impacts on Receiving Waters*. In: *Urban Runoff Pollution*, Torno, H. C; Marsalek, J; Desbordes, M., (eds). Springer Verlag, Berlin.

Hynes, H. B. N. (1960). *The Biology of Polluted Waters*. Liverpool University Press, Liverpool.

Hynes, H. B. N. (1977). *A Key to the Adults and Nymphs of British Stoneflies (Plecoptera)*. 3rd edn, Freshwater Biological Association, Ambleside.

James, W. & Boregowda, S. (1986). *Continuous Mass Balance of Pollutant Build-up Processes*. In: *Urban Runoff Pollution*, H. C. Torno, J. Marsalek, & M. Desbordes, eds., Springer-Verlag, Berlin.

Jubb, S., Hulme, P. R., Guymer, I., & Martin, J. (1998). Considering the Impact of Intermittent Discharges When Modelling Overflows. *Water Science and Technology,* **38**(10), 23-30.

Kedwards, T. J., Blockwell, S. J., Taylor, E. J., & Pascoe, D. (1996). Design of an electronically operated flow-through respirometerand its use to investigate the effects of copper on the respiration rate of the amphipod *Gammarus pulex* (L.). *Bulletin of Environmental Contamination and Toxicology*, **57**, 610-616.

Lake, P. S. (2003. Ecological effects of perturbation by drought in flowing waters, *Freshwater Biology*, **48**, 1161-1172.

Lau, J., Butler, D., & Shutze, M. (2002). Is combined sewer overflow spill frequency / volume a good indicator of receiving water quality impact? *Urban Water*, **4**(2), 181-189.

Law, R. J., Kelly, C., Baker, K., Jones, J., McIntosh, A. D., & Moffat, C. F. (2002). Toxic Equivalency Factors for PAH and their Applicability in Shellfish Pollution Monitoring Studies. *Journal of Environmental Monitoring*, **4**, 383-388.

Lazzari,L; Sperni,L; Bertin,P; Pavoni,B. (2000). Correlation between inorganic (heavy metals) and organic (PCBs and PAHs) micropollutant concentrations during sewage sludge composting processes, *Chemosphere*, **41**, 427-435.

Lee, G. F. & Jones-Lee, A. (1993). Water Quality Impacts of Stormwater Associated Contaminants: Focus on Real Problems, *Water Science and Technology*, **28**(3-5) 231.

Lee, G. F. & Jones-Lee, A. (1995). Issues in Managing Urban Stormwater Runoff Quality, *Water Engineering and Management*, **142**(5), 51-53

Lloyd, D. (1999). *Urban and Post-Industrial Habitats.* Nottinghamshire Wildlife Trust, Nottingham.

Long, E. R. & MacDonald, D. D. (1997). *Effects Range Low and Median, Threshold and Probable Effects Levels.* In: *Use of Sediment Quality Guidelines in the Assessment and Management of Contaminated Sediments*, SETAC Press, Washington D.C.

Longstone, S. (1992). *Report on the Biological Quality of the Blackburn Brook System*, National Rivers Authority, Yorkshire Region.

Ludwig, J. A. & Reynolds, J. F. (1988). *Statistical Ecology: A Primer on Methods and Computing.* John Wiley & Sons, Chichester.

Macan, T. T. (1959). *A Guide to Freshwater Invertebrate Animals.* Longman, Harlow.

MacDonald, D. D., Ingersoll, C. G., & Berger, T. A. (2000). Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. *Archives of Environmental Contamination and Toxicology*, **39**, 20-31.

Makepeace, D. K., Smith, D. W., & Stanley, S. J. (1995). Urban Stormwater Quality: Summary of Contaminant Data. *Environmental Science and Technology*, **25**(2), 93-139.

Malmqvist, B. & Hoffsten, P. (1999). Influence of Drainage From Old Mine Deposits on Benthic Macroinvertebrate Communities in Central Swedish Streams. *Water Research*, **33**(10), 2415-2423.

Malmqvist, P. (1986). *Field Studies of Urban Runoff Quality.* In: *Urban Runoff Pollution*, 1st edn, H. C. Torno, J. Marsalek, & M. Desbordes, (eds). Springer-Verlag, Berlin, pp. 89-102.

Maltby, L. (2000). Pollution and Assessment of Water Quality. Lecture 12 - Habitats and Distributions. http://www.shef.ac.uk/aps/level2modules/aps201/lect12.html . 20-7-0002.

Maltby, L., Forrow, D. M., Boxall, A. B. A., Calow, P., & Betton, C. I. (1995a). The Effects of Motorway Runoff on Freshwater Ecosystems: Field Study. *Environmental Toxicology and Chemistry*, **14**(6), 1079-1092.

Maltby, L., Forrow, D. M., Boxall, A. B. A., Calow, P., & Betton, C. I. (1995b). The Effects of Motorway Runoff on Freshwater Ecosystems: Identifying Major Toxicants. *Environmental Toxicology and Chemistry*, **14**(6), 1093-1101.

Maltby, L., Clayton, S. A., Yu, H., McLoughlin, N., Wood, R. M., & Yin, D. (2000). Using single-species toxicity tests, community level responses, and toxicity identification evaluations to investigate effluent impacts. *Environmental Toxicology and Chemistry*, **19**, 151-157.

Marine Pollution Monitoring Management Group. (1998). *National Monitoring Programme: Survey of the Quality of UK Coastal Waters.* Marine Pollution Monitoring Management Group, Aberdeen.

Mason, C. F. (1996). *Biology of Freshwater Pollution.* Third edn, Longman Limited, Harlow.

Mason, C. F. (2002). *Biology of Freshwater Pollution.* 4th edn, Pearson Education, Harlow.

Maund, S. J., Taylor, E. J., & Pascoe, D. (1992). Population responses of the freshwater amphipod crustacean *Gammarus pulex* (L.) to copper. *Freshwater Biology*, **28**, 29-36.

May, L., Smith, B., & Kirika, A. (2003). *Review of methods, instrumentation and load estimation for the quantification of diffuse pollution.* Diffuse Pollution Initiative Report No. 3.

McCahon, C. P., & Pascoe, D. (1990). Episodic Pollution: Causes, Toxicological Effects and Ecological Significance. *Functional Ecology*, **4**, 375 - 383.

Medeiros, C., Leblanc, R., & Coler, R. A. (1983). An *in-situ* assessment of the acute toxicity of urban runoff to benthic macroinvertebrates. *Environmental Toxicology and Chemistry*, **2**, 119-126.

Mellanby, H. (1965). *Animal Life in Freshwater. A Guide to Freshwater Invertebrates* Methuen, London.

Merian, E. (1991). *Metals and Their Compounds in the Environment.* VCH, Cambridge.

Met Office (2001). *Rules for rainfall observers. The value of rainfall observations.* Meteorological Office, Bracknell.

Meyer, J. L, Paul, M. J. & Taulbee, W. K. (2003). Small Streams in Large Cities: Neglected Links in Urban River Networks. In: Riversymposium, 2003, Brisbane, Australia.

Milne., Mallett, M. J., Clarke, S. J., Flower, S. G., Holmes, D., & Chambers, R. G. (1992). *Intermittent Pollution - Combined Sewer Overflows, Ecotoxicology and Water Quality Standards.* NRA, R & D Note 123.

Mize, S. V. & Deacon, J. R. (2002). *Relations of Benthic Macroinvertebrates to Concentrations of Trace Elements in Water, Streambed Sediments, and Transplanted Briophytes and Stream Habitat Conditions in Nonmining and Mining Areas of the Upper Colorado River Basin, Colorado, 1995-98*, U.S. Geological Survey, Water-Resources Investigations Report 02-4139.

Morrison,G.M.P; Revitt,D.M; Ellis,J.B; Svensson,G; Balmer,P. (1984). Variations of dissolved and suspended solid heavy metals through an urban hydrograph. *Environment Technology. Lett*, **7**(313)

Mouillot, D. & Leprêtre, A. (1999). A comparison of species diversity estimators. *Researches on Population Ecology*, **41**(2), 203-215.

Mullis, R. M., Revitt, D. M., & Shutes, R. B. E. (1996). A Statistical approach for the Assessment of the Toxic Influences on *Gammarus pulex* (Amphipoda) and *Asellus*

aquaticus (Isopoda) Exposed to Urban Aquatic Discharges. *Water Research*, **30**(5), 1237-1243.

Muschack, W. (1990). Pollution of Street Run-Off by Traffic and Local Conditions. *The Science of the Total Environment*, **93**, 419-431.

Myers, C. F., Meek, J., Tuller, J. S., & Weinberg, A. (1985). Nonpoint Sources of Water Pollution. *Journal of Soil and Water Conservation*, **40**(1), 14-18.s

Naden, P., Smith, B., Jarvie, H., Llewellyn, N., Matthiessen, P., Dawson, H., Scarlett, P., & Hornby, D. (2002). *Life in UK Rivers. Methods for the assessment and moitoring of siltation in SAC rivers*. Centre for Ecology & Hydrology, Wallingford.

NAMC. (2002). Aquatic Invertebrate Monitoring - 101. http://www.usu.edu/buglab/bugs101.htm, National Aquatic monitoring Center. 02/10/2002.

New South Wales Environmental Protection Agency. (2001). *How does stormwater pollution affect us?,* www.epa.nsw.gov.au/stormwater/

Novotny, V. (1995). *Nonpoint Pollution and Urban Stormwater Management.* Technomic Publishing Co., Inc, Lancaster.

Novotny, V. & Chesters, G. (1981). *Handbook of Nonpoint Pollution: Sources and Management.* Van Nostrand Reinhold, New York.

Novotny, V. & Olem, H. (1994). *Water Quality: Prevention, Identification and Management of Diffuse Pollution.* 1st edn, Van Nostrand Reinhold, New York.

Novotny, V. & Witte, J. W. (1997). Ascertaining Aquatic Ecological Risks of Urban Stormwater Discharges. *Water Resources*, **31**(10), 2573-2585.

NRDC. (2001). The Causes of Urban Stormwater Pollution. National Resources Defence Council . 2001. 6-9-0001.

Ohio University. Species Diversity. (2002). Department of Environmental and Plant Biology. http://www.plantbio.ohiou.edu/epb/instruct/ecology/LEC5.pdf . 10/01/2004.

Olivieri, V. P., Kruse, C. W., & Kawata, K. (1977). *Microorganisms in Urban Stormwater.* U.S. Environmental Protection Agency, Cincinatti, EPA 600/2-77-087.

Osborne, L. L. & Herricks, E. E. (1980). *Habitat and Water Quality Considerations in Receiving Waters.* ASCE Edition 1: Urban Runoff quality Controls. Reston, Virginia.

Pascoe, D. (1987). *Episodic pollution incidents: experimental studies in the field and laboratory.* In: *Biological Monitoring of Environmental Pollution: Proceedings of the Fourth IUBS International Symposium on Biomonitoring of the State of the Environment (Bioindicators) 6-8 November, 1987, Tokyo, Japan*, M. Yasuno & B. A. Whitton, (eds). Tokai University Press, Tokyo.

Pascoe, D. & Shazili, N. A. M. (1986). Episodic pollution - a comparison of brief and continuous exposure of rainbow trout to cadmium. *Ecotoxicology and Environmental safety*, **12**, 189-198.

Paul, M. J. & Meyer, J. L. (2001) Streams in the Urban Landscape. *Annual Review of Ecology and Systematics*, **32**, 333-365.

Payne, J. A. (1989) *Assessment of the Impact of Discharges From Surface Water Sewers on Receiving Water Quality*, unpublished PhD thesis, Aston University.

Payne, J. A. & Hedges, P. D. (1990). Evaluation of the Impacts of Discharges From Surface water Sewer Outfalls. *Water Science and Technology*, **22**(10-11), 127-135.

Perdikaki, K. & Mason, C. F. (1999). Impact of Road Runoff on Receiving Streams in Eastern England. *Water Research*, **33**(7), 1627-1633.

Persaud, D., Jaagumagi, R., & Hayton, A. (1993). *Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario*, Ontario Ministry of the Environment and Energy, Ontario.

Pires, A. M., Cowx, I. G., & Coelho, M. M. (2000). Benthic macroinvertebrate communities of intermittent streams in the middle reaches of the Guadiana Basin (Portugal). *Hydrobiologia*, **435**, 167-175.

Plotnikoff, R. W. (1998). *Stream Biological Assessments (Benthic Macroinvertebrates) for watershed Analysis: Mid-Sol Duc Watershed Case Study*. Washington State Department of Ecology, Olympia, Washington, Publication No. 98-334.

Power, E. A. & Chapman, P. M. (1992). *Assessing sediment quality*. In: *Sediment Toxicity Assessment*, G. A. Burton, (ed). Lewis Publishers, Ann Arbor.

Quigley, M. (1977). *Invertebrates of Streams and Rivers: a key to identification*. 1st edn, Edward Arnold, London.

Ragavan, A. & Sada, D. W. (2000). *Biomonitoring of Springs*. University of California.

Randall, C. W. & Grizzard, T. 1983, *Runoff Pollution*. In: *Stormwater Management in Urbanizing Areas*. Whipple, W., Grizzard,T., Randall,C.W., Shubinski, R.P., Tucker, L.S., Grigg, N.S. *et al.*, (eds). Prentice Hall, New Jersey.

Rauch,S. & Morrison, G.M. (1999). Platinum uptake by the freshwater isopod *Asellus Aquaticus* in urban rivers. *The Science of the Total Environment*, **235**, 261-268.

Rehwoldt, R., Lasko, L., Shaw, C., & Wirhowski, E. (1973). The Acute Toxicity of Some Heavy Metal Ions Toward Benthic Organisms. *Bulletin of Environmental Contamination and Toxicology*, **10**, 291-294.

Resh, V. H. & Unzicker, J. D. (1975). Water quality monitoring and aquatic organisms: the importance of species identification. *Journal of the Water Pollution Control Federation*, **47**(1), 9-19.

Ricklefs, R. E. & Miller, G. L. (2000). *Ecology*. Fourth edn, Freeman, New York.

Roesner, L. A. (1999). Urban Runoff Pollution - Summary Thoughts - The State of Practice Today and for the 21st Century. *Water Science and Technology*, **39**(12), 353-360.

Saget, A., Chebbo, G., & Bertrand-Krajewski, J. (1996). The First Flush in Sewer Systems. *Water Science and Technology*, **33**(9), 101-108.

Saget, A., Gromaire-Mertz, M. C., Deutsch, J. C., & Chebbo, G. (1998). *Extent of Pollution in Urban Wet Weather Discharges.* In: *Hydrology in a Changing Environment*, Wiley & Sons, pp. 415-424.

Salomons, W., Förstner, U., & Mader, P. (1995). *Heavy Metals: Problems and Solutions.* Springer, London.

Sartor, J. D. & Boyd, G. B. (1972). *Water Pollution Aspects of Street Surface Contaminants.* United States Environmental Protection Agency, EPA-R2-72-081. Washington D. C.

Savage, N. L. & Rabe, F. W. (1973). The effects of mine and domestic wastes on macroinvertebrate community structure in the Coeur d'Alene River. *Northwest Science*, **47**, 159-168.

SCA. (1988). *The Determination of pH in Low Ionic Strength Waters.* HMSO, London.

Schueler, T. R. (1987). *Controlling Urban Runoff: A Practical Manual for Planning and Designing Urban BMPs.* Washington Metropolitan Water Resources Planning Board, Washington, DC.

Scottish Executive. (2004). Protecting Scotland's Water Environment: Water Framework Directive. http://www.scotland.gov.uk/about/ERADEN/WEU/00017316/Home.aspx .17/7/2004.

Seager, J. & Maltby, L. (1989). Assessing the impact of episodic pollution. *Hydrobiologia*, **188/189**, 633-640.

Seager, J. & Abrahams, R. G. (1990). The Impact of Storm Sewage Discharges on the Ecology of a Small Urban River. *Water Science and Technology*, **22**(10-11),163-171.

SEPA. (1997). *A Guide to Sustainable Urban Drainage.* Scottish Environmental Protection Agency, Stirling.

SEPA. (2003). *National Water Quality Classification 2003.* Scottish Environmental Protection Agency, Stirling.

SEPA. (2003a). Diffuse Pollution Initiative. http://www.sepa.org.uk/dpi/, 19/9/2003a.

SEPA. (2003b). Diffuse Pollution Initiative: Resources: Report 7. http://www.sepa.org.uk/dpi/resources/dpi_reports/dpi_007.pdf , 1-19, 18/9/2003

SEPA. (2004). Environmental Data: Classification Schemes.

http://www.sepa.org.uk/data/classification/river_classification.htm, 21/7/2004.

Shaw, E. M. (1996). *Hydrology in Practice.* 3rd edn, Chapman Hall, London.

Shepp, D. L. (1996). *Petroleum Hydrocarbon Concentrations Observed in Runoff From Discrete, Urbanized Automotive-Intensive Land Uses.* Office of Wetlands, Oceans & Watersheds.

Shutes, B., Ellis, B., Revitt, M., & Bascombe, A. (1992). The use of freshwater invertebrates for th eassessment of metal pollution in urban receiving waters. In: *Ecotoxicology of metals in Invertebrates.* Dallinger, R & Rainbow, P. (eds). Lewis Publishers, Boca Raton, pp. 201-222.

Shutes, R. B. E. (1984). The Influence of Surface Runoff on the Macro-invertebrate Fauna of an Urban Stream. *The Science of the Total Environment*, **33**, 271-282.

Solbe, J. F. d. L. G. (1977). *Water quality, fish and invertebratesin a zinc-polluted stream.* In: *Biological Monitoring of Inland fisheries.* Alabaster, J. S. (ed). Applied Science Publishers, London, pp. 97-105.

South Yorkshire Forest Partnership. (2002). *South Yorkshire Forest Plan.* South Yorkshire Forest Partnership, Sheffield.

Spehar, R. L. & Fiandt, J. T. (1986). Acute and chronic effects of water quality criteria-based metal mixtures to three aquatic species. *Environmental Toxicology and Chemistry*, **5**, 917-931.

Sriyaraj, K. & Shutes, R. B. E. (2001). An assessment of the impact of motorway runoff on a pond, wetland and stream. *Environment International*, **26**, 433-439.

Standing Committee of Analysts. (1988). *Ammonia in Waters: Methods for the examination of waters and associated materials.* HMSO, London.

Standing Committee of Analysts. (1988). *Water quality - Part 2: Physical, chemical and biochemical methods - Section 2.34 Method for the determination of the chemical oxygen demand.* HMSO, London.

Standing Committee of Analysts. (1992). *Method for determination of dissolved oxygen in water: electrochemical probe method.* HMSO, London.

Standing Committee of Analysts. (1996a). *Water quality. Determination of suspended solids. Method by filtration through glass fibre filters.* HMSO, London.

Standing Committee of Analysts British Standards Institute. (1996b). *Water quality - Sampling - Guidance on the preservation and handling of samples.* HMSO, London.

Standing Committee of Analysts. (1988). *Water quality - Determination of biochemical oxygen demand after n days (BODn) - Part 2*: Method for undiluted samples. HMSO, London.

Standing Committee of Analysts. (1999). *Water quality Part 6: Sampling- Section 6.15 Guidance on preservation and handling of sludge and sediment samples.* HMSO, London.

Stroud Center. (2002). *Leaf Pack Network: Macroinvertebrtaes.* http://www.stroudcenter.org/lpn/more/macro.htm, 17/8/2002.

Tebbutt, T. H. Y. (1998). *Principles of Water quality Control.* 5th edn, Butterworth-Heinemann, Oxford.

Terstrep, M. L., Noel, D. C., & Bender, G. M. (1986). Sources of Pollutants - Do We Know Enough?. *Urban Runoff Quality - Impact and Quality Enhancement Technology.* Proceedings of an Engineering Foudation Conference, New England College, Henniker, New Hampshire, 23rd June 1986.

Thurston, R. V., Russo, R. C., & Vinogradov, G. A. (1981). Ammonia toxicity to fishes. The effect of pH on the toxicity of the un-ionized ammonia species. *Environmental Science and Technology*, **15**, 837-840.

Tomasso, J. R., Goudie, C. A., Simco, B. A., & Davis, K. B. (1980). Effects of environmental pH and calcium on ammonia toxicity in channel catfish. *Transactions of the American Fisheries Society*, **109**, 229-234.

Transport Research Laboratory, DWW (Netherlands), VTI (Sweden), VTT (Finland), DRI (Denmark), LCPC (France), & LNEC (Portugal). (2002). *Pollution from Roads and Vehicles and Dispersal to the Local Environment: Final report and Handbook.* European Commission, POLMIT RO-97-SC.1027.

Unidata. (2000). *STARFLOW Ultrasonic Doppler Instrument User's Manual: Revision F*, Unidata, O'Connor, Western Australia.

U.S. EPA. (1983). *Final Report of the Nationwide Urban Runoff Programme.* Environmental Protection Agency US, Washington D. C., 20460.

U.S.EPA. (1984). *Report to Congress: Nonpoint Source Pollution in the U.S.*, Water Planning Division, U.S. EPA, Washington, DC.

U.S.EPA. (1986). *Quality Criteria for Water*, Office of Water, U.S. Environmental Protection Agency, Washington D.C, USA, EPA 440/5-86-001.

U.S.EPA. (1990). *National Water Quality Inventory 1988 Report to Congress.* Washington D.C, EPA/440/4-90/003.

U.S. EPA. (1996). *Method 3540C Soxhlet Extraction.* U.S. Environmental Protection Agency, Washington D.C.

U.S. EPA. (2002). *Rapid Bioassessment Protocols For Use in Streams and Rivers: Periphyton, Benthic, Macroinvertebrates, and Fish*, 2nd edn. http://wilkes.edu/~eqc/macroinv.htm . Wilkes University Center for Environmental Quality GeoEnvironmental Science and Engineering Department. 1/10/2002.

U.S. EPA. (2003). *Method 610 - Polynuclear Aromatic Hydrocarbons.* U.S. Environmental Protection Agency, Washington D.C.

U.S.Fish and Wildlife Service. (2004). *Final Report on Characterization of Fish and Macroinvertebrates in Willow Creek*, Willow Creek Reclamation Committee, Creede, Colorado.

UK Biodiversity Partnership. (1994). *Biodiversity The UK Action Plan.* HMSO, London.

Van-Buren, M. A., Watt, W. E., Marsalek, J., & Anderson, B. C. (1999). Thermal Enhancement of Stormwater Runoff by Paved Surfaces. *Water Resources*, **34**(4), 1359-1371.

van der Heijden, T. R. J. M., Lijklema, L., & Aalderink, R. H. (1986). *A Statistical Methodology for the Assessment of Water Quality Effects of Stormwater Discharges.* In: *Urban Runoff Pollution*, H. C. Torno, J. Marsalek, & M. Desbordes, (eds). Springer-Verlag, Heidelberg, pp. 305-324.

van Metre, P. C., Mahler, B. J., & Furlong, E. T. (2000). Urban Sprawl Leaves Its PAH Signature, *Environmental Science and Technology*, **34**(19), 4064-4070.

Wagner, A. & Geiger, W. F. (1996). "New Criteria for Stormwater Discharges Into Urban Streams", *Water Science and Technology*, **34**(3-4), 41-48.

Walker, W. J., McNutt, R. P., & Maslanka, C. K. (1999). The Potential Contribution of Urban Runoff to Surface Sediments of The Passaic River: Sources and Chemical Characteristics, *Chemosphere*, **38**(2), 363-377.

Wallingford Software & Anjou Recherche. (1999). *Hydroworks. 5.0 [Build 034],* Wallingford Software.

Walley, W. J. & Hawkes, H. A. (1996). A Computer-Based Reappraisal of the Biological Monitoring Working Party Score System Using Data From the1990 River Quality Survey of England and Wales, *Water Research* , **30**(9), 2086-2094.

Warn, T. (2002). *Environment Drivers for AMP 4* , Environment Agency, Bristol.

Weibel, S. R., Weidner, R. B., Cohen, J. M., & Christianson, A. G. (1966). Pesticides and Other Contaminants in Rainfall and Runoff. *Journal of the American Water Works Association*, **58**(8), 1075-1084.

Welch, E. B. (1992). *Ecological Effects of Wastewater: Applied limnology and pollutant effects.* 2nd edn, Chapman & hall, London.

Wendell Cox Consultancy. (2001). Demographia, http://www.demographia.com/db-ikcities.htm, 14/02/2002.

Wiederholm, T. (1984). Responses of Aquatic Insects to Environmental Pollution. In: *The Ecology of Aquatic Insects*, V. H. Resh & D. M. Rosenberg, (eds). Praeger, New York, pp. 508-557.

Wilkinson, R. (1955). Quality of Rainfall Runoff Water from a Housing Estate. *Journal of the Institution of Public Health Engineers*, **55**, 70-84.

Williams, K. A., Green, D. W. J., & Pascoe, D. (1985). Studies on the acute toxicity of pollutants to freshwater macroinvertebrates 1. Cadmium. *Archiv fur Hydrobiologie*, **102**, 461-471.

Williams, P., Whitfield, M., Biggs, J., Bray, S., Fox, G., Nicolet, P., & Sear, D. (2003). Comparative biodiversity of rivers, streams, ditches and ponds in an agricultural landscape in Southern England. *Biological Conservation*, **115**(2), 329-341.

Wilson, C., Clarke, R., D'Arcy, B. J., Heal, K. V., & Wright, P. W. (2003). *Persistent Pollutants Urban Rivers Sediment Survey: Implications For Pollution Control.* Diffuse Pollution Conference, Dublin, 94-99.

Wilson, P. J., (1999). *Pollution from highway runoff: the Highways Agency approach.* SCI Lecture Paper Series, 1-9, Highways Agency, London.

Winner, R. W., Boesel, M. W., & Farrell, M. P. (1980). Insect Community Structure as an Index of Heavy Metal Pollution in Lotic Ecosystems. *Canadian Journal of Fisheries and Aquatic Science*, **37**, 647-655.

Winner, R. W., Van Dyke, S., Caris, N., & Farrell, M. P. (1975). Response of the macroinvertebrate fauna to a copper gradient in an experimentally-polluted stream. *Internationale Vereinigung fur Theoretische und Angewandte Limnologie Verhandlungen*, **19**, 2121-2127.

Wright, J. F., Furse, M. T. & Armitage, P. D. (1993). RIVPACS-techniques for evaluating the biological quality of rivers in the UK. *European Water Pollution Control*, 3, 15-25.

Wright, J. F., Furse, M. T., & Armitage, P. D. (1994). *Use of macroinvertebrate communities to detect environmental stress in running waters.* In: *Water Quality and Stress Indicators in Marine and Freshwater Ecosystems: Linking Levels of Organisation (Individuals, Populations, Communities).* Joint Associations specialised conference at Napier University, Edingburgh, 6-7, September, 1993, D. W. Sutcliffe, ed., Freshwater Biological Association, pp. 15-34.

Wright, P. (2002). *Invertebrates and the Pollution of Rivers.* Caithness Field Club Bulletin, October, 2002.
http://www.caithness.org/caithnessfieldclub/bulletins/1980/octob.

Yoccoz, N. G., Nichols, J. D., & Boulinier, T. (2001). Monitoring of biological diversity in space and time. *Trends in Ecology and Evolution*, **16**(8), 446-453.

Yorkshire Water. (2002). Map SK 3396SE. Yorkshire Water Records Services. Western House, Bradford, BD6 2LZ.

Zhang, W. (2003). Nanoscale Iron Particles for Environmental Remediation: An Overview. *Journal of Nanoparticle Research*, **5**(3), 323-332.

Appendix I

STARFLOW

Velocity: The manufacturer's specifications claim a resolution of 1 mm / s with an uncertainty of ± 2% of measured velocity. Laboratory evaluations in 1 ft and 8.5 ft wide rectangular flumes by Vermeyen, (2002), produced velocity measurements that were consistently 24 % greater than the average channel velocity. This degree of error is clearly undesirable but the consistency in the percentage error suggested that the STARFLOW should have a stable calibration over a range of flows and depths. Laboratory tests by the author using an OTT 10152 current meter at 0.6 depth to approximate average channel velocity, produced readings to within 1% of the STARFLOW readings for velocities greater than 0.16 m/s. However, tests on velocities lower than 0.110 m/s produced results on average, 36% lower than those produced by the STARFLOW, mirroring tests by Vermeyen (ibid.). This reinforced the understood need to calibrate in the field.

Depth: The manufacturers specifications claim an accuracy of ± 0.25% of calibrated lower range, i.e. up to a depth of 1.006 m, equating to an uncertainty of 0.0025 m. In the laboratory evaluation carried out by Vermeyen (2001), depth measurements by the STARFLOW were on average, 1.37% greater than the known stage measurements. However, if these systematic errors were quantified by field calibration, corrections could be applied during data processing. At this juncture it is necessary to point out that ripples on the water surface will add a degree of uncertainty to the depth measurements obtained. Laboratory tests by the author showed that the STARFLOW under-predicted depth by an average of 2.0% over a range of depths up to 0.280 m.

Discharge: As with the average channel velocities recorded by Vermeyen, the STARFLOW consistently computed discharges that were 24 % greater than the known discharge for tests conducted in 1 and 8.5 ft flumes. Further, to ensure accuracy of STARFLOW measurement and prior to placement in-situ, the unit was tested by the author under laboratory conditions in a 4-inch flume at a known depth and velocity, after being programmed with the user defined area rating scale. This test highlighted the limitations of the STARFLOW software in respect of the user-defined rating scheme. The STARFLOW only accepts ratings for 1m, 2m, 5m and 10m stage channels. Consequently, the unit produced a range of values deduced from an assumed maximum stage of 2m multiplied by areal values based on a maximum stage of 1.232m [the site culvert]. This was adjusted by changing the cumulative stage (y) values to multiples of 2mm whilst retaining values of x (width) from the original rating. After the stage value of 1.232m was reached, remaining values were entered as 0. Further laboratory tests gave consistently low readings, approximately 50% smaller than expected for both cross-sectional area and discharge. Consequently the STARFLOW was tested over a period of 5 hours at different depths and the discrepancy analysed for level of consistency. Overall, the STARFLOW produced readings lower than those programmed by a factor of 2.013. Applying this correction produced results to within 2 % of that expected. Weighed tests in the flume at depths ranging from 0.09 to 0.2 m and velocities in the range 0.13 to 0.29 m/s, produced discharges that were on average, 0.18 l/s greater than the STARFLOW.

Appendix II

Biomonitoring sheets for use with invertebrate sampling

LIFE		**Comments**
BMWP		
ASPT		
No. Families		
Habitat **Rich / poor**		

Channel							
Average width (m)		Average sampling depth (cm)		Average channel depth (cm)			
Bedrock %		Cobbles %		Gravel %		Silt %	
Boulders %		Pebbles %		Sand %		Clay %	

Detritus	None	Local %	Widespread %	Extensive %	
Sewage litter	None	Local %	Widespread %	Gross %	
Bed stability	Solid %	Stable %	Unstable %	Loose %	Soft %

Rubbish		**Oil film**	
Eroding %		Depositing %	

Habitat	Torrent %	Riffle %	Run %	Glide %
	Slack %	Pool %	Ponded reach %	Ditch %

Sewage / Ochre	None %	Local %	Widespread %	Extensive %
Sewage Fungus	None %	Local %	Widespread %	Extensive %
Ochre	None %	Local %	Widespread %	Extensive %

Algae / Macrophytes / Mosses				
Filamentous algae	None %	Local %	Widespread %	Extensive %
Non-filamentous algae	None %	Local %	Widespread %	Extensive %
Mosses	None %	Local %	Widespread %	Extensive %

Macrophyte species present

Banks / land					
Primary	Broad leaved / Mixed wood	Conifer wood	Scrub pasture	Urban	Wetland
Secondary	Broad leaved / Mixed wood	Conifer wood	Scrub pasture	Urban	Wetland

Comments (e.g. fish species, weather etc.)

Appendix III

Chemical General Quality Assessment

Grades of river quality for the chemical GQA. From Environment Agency, 2001.

Chemical grade		Likely uses and characteristics
A	Very good	All abstractions Very good salmonid fisheries Cyprinid fisheries
B	Good	All abstractions Salmonid fisheries Cyprinid fisheries Ecosystems at or close to natural
C	Fairly good	Potable supply after advanced treatment other abstractions Good cyprinid fisheries Natural ecosystems, or those corresponding to good cyprinid fisheries
D	Fair	Potable supply after advanced treatment Other abstractions Fair cyprinid fisheries Impacted ecosystems
E	Poor	Low grade abstraction for industry Fish absent or sporadically present, vulnerable to pollution Impoverished ecosystems
F	Bad	Very polluted rivers which may cause nuisance severely restricted ecosystems

Appendix IV

Biological General Quality Assessment

General Quality Assessment system of biological grading. From: Environment Agency, 2003.

Grade	Outline description
A -very good	The biology similar to (or better than) that expected for an average, unpolluted river of this size, type and location. There is a high diversity of families, usually with several species in each. It is rare to find dominance of any one family.
B - good	The biology shows minor differences from Grade - 'a' and falls a little short of that expected for an unpolluted river of this size, type and location. there may be a small reduction in the number of families that are sensitive to pollution, and a moderate increase in the number of families that tolerate pollution (like worms and midges). this may indicate the first signs of organic pollution.
C - fairly good	The biology is worse than expected for an unpolluted river of this size, type and location. Many of the sensitive families are absent, or the number of individuals reduced and in many cases there is a marked rise in the numbers of individuals in the families that tolerate pollution.
D - fair	The biology shows considerable differences from that expected for an unpolluted river of this size, type and location. Sensitive families are scarce and contain only small numbers of individuals. There may be a range of those families that tolerate pollution and some of these may have high numbers of individuals.
E - poor	The biology is restricted to animals that tolerate pollution with some families dominant in terms of the numbers of individuals. Sensitive families will be rare or absent.
F - bad	The biology is limited to a small number of very tolerant families, often only worms, midge larvae, leeches and the water hog-louse. These may be present in very high numbers, but even these may be missing if the pollution is toxic. In the very worst case, ther may be no life present in the river.

BMWP

The BMWP score is a scoring system that can be used to reflect the impact of organic pollution. Each group or family of macro-invertebrates sampled is allocated a score between 1 and 10 according to their sensitivity to environmental changes, with the most sensitive species being allocated a 10 and the least sensitive a 1. The sum of the scores for each family gives a BMWP score for each site (Bartram & Balance, 1996).

BMWPASPT

The BMWP Average Score Per Taxon is calculated for each site, by dividing the BMWP score by the total number of taxa (families) in each sample, the result being independent of sample size and as a consequence, providing more information from less effort. The ASPT is less influenced by season than the BMWP score, so that samples taken in any season will provide consistent estimates of ASPT. (Mason, 1996).

A BMWP score of >100 with an ASPT score of >4 generally indicates good water quality.

RIVPACS

The River Invertebrate Prediction and Classification Scheme (RIVPACS) is a software package in common use with the Environment Agency and the Scottish Environmental Protection Agency in environmental assessment, typically in measuring the effects of river regulation on faunal communities (Beech, 2001). Its main use is in predicting the probability of likely species at any given site, from known environmental variables such as channel slope and substrate type, against which the effects of changes in water quality can be assessed. The system in addition to species prediction also predicts BMWP, average number of taxa and BMWPASPT values. Both ASPT and number of taxa in the samples collected can be divided by the equivalent values predicted by RIVPACS so that they are expressed as the proportion of their value when environmental quality is good. These proportional values are called Ecological quality Indices (EQIs).

Appendix V

General Quality Assessment (chemistry) and physico chemical results

Biochemical oxygen demand (ATU) data (mg l^{-1})

Site	1	2	3	4
Date				
07/02/2002	1.75	1.35	4.6	3.65
21/02/2002	2.95	2.1	1.85	4.38
07/03/2002	1.05	1.35	3.18	3.7
21/03/2002	1.3	1.4	2.45	4.5
04/04/2002	0.45	2	3.3	5
18/04/2002	1.5	3.35	2.7	6.1
02/05/2002	1.15	1.2	2.4	2.7
16/05/2002	1.6	1.1	1.2	4.8
30/05/2002	1	1.35	1.1	1.9
13/06/2002	1.4	2.1	2.5	2.1
27/06/2002	1.3	1.2	2.2	2.8
11/07/2002	0.9	2.3	2.4	5.2
25/07/2002	1.5	1.1	1.7	1.6
05/09/2002	1	1.5	1.8	2.5
20/09/2002	1	1	1.8	1.1
04/10/2002	1	1.8	2.6	3
17/10/2002	2.15	3	1.75	1.75
31/10/2002	0.6	0.3	0.8	1.3
14/11/2002	1	1.1	0.75	1.3
27/11/2002	1.3	1.7	1.75	2.45
19/12/2002	1.6	2.05	2.3	2.4
10/01/2003	2.3	3.1	1.9	2.1
17/01/2003	1.3	1.5	1.75	2.4
28/01/2003	1.25	2.1	1.4	2.5
04/02/2003	1.05	1.2	2.25	1.5
28/02/2003	0.45	0.95	1.45	1.6
14/03/2003	2.8	1.45	1.65	4.4
27/03/2003	2.3	2.1	2.4	5.1
30/04/2003	2.1	1.6	3.8	3.2
12/06/2003	1.2	1.2	2	3
03/06/2003	1.3	2	2.2	2.8
26/06/2003	0.5	0.9	3.8	1.5
09/07/2003	2.2	1.9	3.3	2.1
18/07/2003	0.8	1.7	2.9	2.5
06/11/2003	0.8	1.1	3.4	3.5
20/11/2003	0.4	1.5	1.4	2.7
27/11/2003	0.4	0.4	2.5	5

Suspended sediment data (mg l^{-1})

Site	1	2	3	4
Date				
07/02/2002	36.8	27.2	9.2	76
21/02/2002	18	15.2	6	74.4
07/03/2002	12	30	14	25
21/03/2002	8	6	2	16
04/04/2002	7	9	6	12
18/04/2002	7	2	2	6
02/05/2002	77	7	6	5
16/05/2002	17.5	7	11	4.5
30/05/2002	20	14	6	2
13/06/2002	8	13	4	2
27/06/2002	12	10	6	4
11/07/2002	7	5	5	2
25/07/2002	7	19	7	7
05/09/2002	4	23	4	4
20/09/2002	4	6	8	4
04/10/2002	4	3	6	2
17/10/2002	*	*	*	*
31/10/2002	9.5	33	18	8
14/11/2002	11.5	15.5	17	17.5
27/11/2002	9	14	7.5	6.5
19/12/2002	1.5	26	29.5	7.5
10/01/2003	44.5	32.3	49.5	41
17/01/2003	16.5	15	12	8.3
28/01/2003	8.5	23.5	16.5	12.5
04/02/2003	2.5	14	5.5	3.5
28/02/2003	11.5	4.5	1	4
14/03/2003	3.5	10	7	7
27/03/2003	5	8	4	4
30/04/2003	8.3	23	16	5.3
12/06/2003	7	4.3	6.3	6
03/06/2003	10	5	6	6
26/06/2003	3	5	3	1.5
09/07/2003	7.5	10.3	9.3	8
18/07/2003	7	11	9	5
06/11/2003	3	3.67	4	3
20/11/2003	5	9	4	2
27/11/2003	3	3	13	3

Dissolved oxygen data (percentage saturation)

Site	1	2	3	4
Date				
07/02/2002	106	105	100	103.5
21/02/2002	95.7	109	94	94.6
07/03/2002	93	89	86.4	87.2
21/03/2002	98	98	97	95
04/04/2002	104	101	102	118
18/04/2002	100	97	93	95
02/05/2002	92	91	89	84
16/05/2002	90	89	88	79.3
30/05/2002	96	90.6	90.8	80.2
13/06/2002	96	92	91	82
27/06/2002	94	90.7	89.6	81
11/07/2002	84.5	81.2	97.4	81
25/07/2002	105.5	104.6	100.1	110
05/09/2002	89	85	95	78
20/09/2002	97	95	87	65
04/10/2002	98	98	95	65
17/10/2002	96	94	93	87
31/10/2002	97	92	94	88
14/11/2002	98.9	97	97	93
27/11/2002	95.2	93	93	89
19/12/2002	93	94	93	90
10/01/2003	90.2	93.4	88.2	84.3
17/01/2003	92.4	90.2	86.8	82.2
28/01/2003	93.3	93.5	92.8	87.4
04/02/2003	89	89.7	89.3	85.6
28/02/2003	99	99	100	94.4
14/03/2003	97.7	96.5	96.9	92.6
27/03/2003	100.3	101.8	113.2	102.3
30/04/2003	96.5	95.2	95.5	84
12/06/2003	89.6	86	84.3	75.2
03/06/2003	93	89	83	55
26/06/2003	105	100	79	66
09/07/2003	88.9	84.9	82.3	76
18/07/2003	84.6	85	84.3	76
06/11/2003	74.2	73.3	67.4	46.7
20/11/2003	84	88	85	57
27/11/2003	82	83	76	70

Ammonia data (mg N l^{-1})

Site	1	2	3	4
Date				
07/02/2002	*	*	*	*
21/02/2002	0.39	0.32	0.52	**2.32**
07/03/2002	0.25	0.38	0.34	0.38
21/03/2002	0.15	0.16	0.16	0.61
04/04/2002	0.085	0.11	0.085	0.29
18/04/2002	0.22	0.44	0.1	0.88
02/05/2002	0.05	0.13	0.12	0.35
16/05/2002	0.06	0.09	0.17	0.09
30/05/2002	0.76	0.11	0.12	0.19
13/06/2002	0	0.06	0	0.22
27/06/2002	0.17	0.1	0.06	0.09
11/07/2002	0.328	0.158	0.109	0.17
25/07/2002	0.0364	0.36	0.134	0.22
05/09/2002	0.024	0.401	0.304	0.304
20/09/2002	0.08	0.12	0.34	0.08
04/10/2002	0.085	0.267	0.643	2.562
17/10/2002	0.182	0	0.024	0.122
31/10/2002	0.061	0.073	0.121	0.036
14/11/2002	0.1214	0.085	0.1214	0.1093
27/11/2002	0.061	0.085	0.109	0.134
19/12/2002	0.0728	0.158	0.097	0.134
10/01/2003	0.0121	0.0243	0.1214	0.971
17/01/2003	0.09	0.1214	0.134	0.34
28/01/2003	0.1093	0.607	0.0724	0.0724
04/02/2003	0	0.085	0.085	0.158
28/02/2003	0.012	0.109	0.109	0.255
14/03/2003	0.0486	0.0607	0.0243	0.0849
27/03/2003	0.049	0.06	0.133	0.097
30/04/2003	0.146	0.182	0.061	0.316
12/06/2003	0.0607	0.0607	0.219	0.182
03/06/2003	0.073	0.158	0.206	0.413
26/06/2003	0.0607	0.255	0.534	0.352
09/07/2003	0.0364	0.243	0.243	0.134
18/07/2003	0.0364	0.243	0.255	0.267
06/11/2003	0.0607	0.158	0.971	0.267
20/11/2003	0.109	0.109	0.255	0.765
27/11/2003	0.146	0.291	1.141	0.304

Chemical oxygen demand data (mg l^{-1})

Site	1	2	3	4
Date				
07/02/2002	*	*	*	*
21/02/2002	*	*	*	*
07/03/2002	*	*	*	*
21/03/2002	*	*	*	*
04/04/2002	85	111	93	**137**
18/04/2002	44	102	58	95
02/05/2002	86	25	14	7
16/05/2002	7.4	18.5	**144.4**	64.2
30/05/2002	22.6	20.7	60.2	57.5
13/06/2002	74.6	55.2	52.2	33.6
27/06/2002	27.3	32.9	57.2	44.6
11/07/2002	24.8	28.4	21.3	14.2
25/07/2002	23.8	14	16.6	19
05/09/2002	6.94	20.83	41.66	13.88
20/09/2002	24.65	21.13	42.25	30.99
04/10/2002	14.2	21.3	7.1	28.4
17/10/2002	16.2	30.7	84.1	22.62
31/10/2002	5.6	36	18.4	10.4
14/11/2002	3.8	7.6	3.8	15.19
27/11/2002	5.8	13.5	7.67	11.75
19/12/2002	3.38	10.14	6.76	2.03
10/01/2003	36	32.5	40.94	25.27
17/01/2003	6.8	10.4	7.2	14.5
28/01/2003	4.33	5.76	9.36	20.16
04/02/2003	6.9	3.45	3.45	13.8
28/02/2003	2.35	4.7	5.97	10.4
14/03/2003	5.71	8.57	8.57	25
27/03/2003	13.9	6.99	6.99	41.95
30/04/2003	6.99	13.99	17.48	48.95
12/06/2003	3.38	20.27	20.27	27.03
03/06/2003	6.87	13.75	20.62	54.98
26/06/2003	0	25.83	7.38	44.28
09/07/2003	6.85	10.27	27.4	13.7
18/07/2003	10.34	10.34	6.89	20.69
06/11/2003	3.33	20	0	10
20/11/2003	12.99	29.22	0	38.96
27/11/2003	20.13	26.85	6.71	20.13

pH data

Time	1	2	3	4
Date				
18/04/2002	8.02	7.94	7.78	7.94
02/05/2002	7.97	7.85	7.87	7.82
16/05/2002	7.87	7.99	7.92	7.89
30/05/2002	7.92	8.07	7.79	7.82
13/06/2002	8.15	8.02	7.99	7.96
27/06/2002	8.05	8.02	7.93	7.92
11/07/2002	7.9	8	7.89	7.99
25/07/2002	8.03	8.12	8.09	7.91
05/09/2002	8.42	8.28	8.2	8.27
20/09/2002	8.08	8.03	8.02	8.02
04/10/2002	8.15	8.16	8.12	8.05
17/10/2002	7.25	7.01	7.08	7.7
31/10/2002	8.4	8.34	8.3	8.5
14/11/2002	7.53	8.42	8.4	8.54
27/11/2002	7.86	7.92	8.01	8.21
19/12/2002	7.94	7.97	7.91	7.87
10/01/2003	8.75	8.26	8.2	8.2
17/01/2003	8.1	7.92	8	8.03
28/01/2003	8	7.89	7.9	7.95
04/02/2003	8.18	8.01	8.02	8.04
28/02/2003	8.08	8.14	8.04	8.08
14/03/2003	7.83	7.84	7.78	7.81
27/03/2003	7.81	7.88	7.78	7.69
30/04/2003	7.94	7.93	7.81	7.77
12/06/2003	7.87	7.52	7.71	7.72
03/06/2003	7.93	7.75	7.71	7.58
26/06/2003	8.19	7.94	7.78	7.72
09/07/2003	7.96	7.78	7.69	7.78
18/07/2003	8.14	7.9	7.98	7.93
06/11/2003	7.72	7.76	7.86	7.45
20/11/2003	7.26	7.41	7.58	7.25
27/11/2003	7.4	7.3	7.37	7.52

Metal	Criterion (µg l -1)	Site 1	CCU	Site 2	CCU	Site 3	CCU	Site 4	CCU
Al	87	8.060	0.093	0.619	0.007	6.470	0.074	13.690	0.157
Cd	0.32	0.067	0.208	0.188	0.588	0.169	0.528	0.114	0.356
Cu	11.94	1.104	0.092	12.720	1.065	4.046	0.339	4.882	0.409
Ni	69	0.220	0.003	0.392	0.006	0.896	0.013	0.889	0.013
Pb	3.6	2.224	0.618	2.480	0.689	4.448	1.236	8.885	2.468
Fe	1000	35.500	0.036	11.240	0.011	46.350	0.046	41.650	0.042
Zn	157	3.660	0.023	6.005	0.038	5.335	0.034	5.885	0.037
Mn	1000	32.150	0.032	80.600	0.081	248.700	0.249	131.300	0.131
			1.105		**2.404**		**2.519**		**3.614**

Winter CCU scores.

Metal	Criterion (µg l -1)	Site a	CCU	Site d	CCU	Site e	CCU	Site f	CCU	Site g	CCU
Al	87	11.570	0.133	370.200	4.255	<lod	<lod	0.752	0.009	<lod	<lod
Cd	0.32	0.098	0.305	0.686	2.144	0.621	1.942	0.533	1.665	0.500	1.563
Cu	11.94	<lod	<lod	6.810	0.570	0.636	0.053	1.107	0.093	1.290	0.108
Ni	69	1.250	0.018	2.346	0.034	1.832	0.027	1.797	0.026	2.129	0.031
Pb	3.6	2.357	0.655	33.820	9.394	33.460	9.294	33.400	9.278	33.280	9.244
Fe	1000	31.110	0.031	619.000	0.619	521.000	0.521	219.000	0.219	79.700	0.080
Zn	157	1.410	0.009	1.242	0.008	0.406	0.003	0.721	0.005	1.094	0.007
Mn	1000	<lod	<lod	9.908	0.010	20.620	0.021	5.645	0.006	0.591	0.001
			1.151		**17.035**		**11.860**		**11.299**		**11.034**

Summer CCU scores.

Appendix VII

Invertebrate tables

Site A (species richness = 22) Spring 2003

	n	P*i*	P_i^2	P*i* ln*P*i
Planaridae	4.00	0.0101	0.0001	-0.0464
Oligochaeta	38.00	0.0960	0.0092	-0.2249
Glossiphonidae	0.00	0.0000	0.0000	0.0000
Erpobdellidae	0.00	0.0000	0.0000	0.0000
Gammaridae	66.00	0.1667	0.0278	-0.2986
Asellidae	0.00	0.0000	0.0000	0.0000
Heptagenidae	55.00	0.1389	0.0193	-0.2742
Baetidae	59.00	0.1490	0.0222	-0.2837
Leuctridae	46.00	0.1162	0.0135	-0.2501
Taeniopterygidae	16.00	0.0404	0.0016	-0.1296
Perlodidae	4.00	0.0101	0.0001	-0.0464
Chloroperlidae	11.00	0.0278	0.0008	-0.0995
Nemouridae	39.00	0.0985	0.0097	-0.2283
Leptoceridae	2.00	0.0051	0.0000	-0.0267
Lepidostomatidae	0.00	0.0000	0.0000	0.0000
Sericostomatidae	3.00	0.0076	0.0001	-0.0370
Glossosomatidae	0.00	0.0000	0.0000	0.0000
Philopotamidae	0.00	0.0000	0.0000	0.0000
Odontoceridae	0.00	0.0000	0.0000	0.0000
Rhyacophilidae	2.00	0.0051	0.0000	-0.0267
Polycentropodidae	12.00	0.0303	0.0009	-0.1060
Limnephilidae	3.00	0.0076	0.0001	-0.0370
Hydropsychidae	4.00	0.0101	0.0001	-0.0464
Dytiscidae	0.00	0.0000	0.0000	0.0000
Hygrobidae	0.00	0.0000	0.0000	0.0000
Elmidae	1.00	0.0025	0.0000	-0.0151
Tipulidae	0.00	0.0000	0.0000	0.0000
Simulidae	9.00	0.0227	0.0005	-0.0860
Chironomidae	8.00	0.0202	0.0004	-0.0788
Ancylidae	0.00	0.0000	0.0000	0.0000
Sphaeridae	0.00	0.0000	0.0000	0.0000
Valvatidae	0.00	0.0000	0.0000	0.0000
Hydrobidae	3.00	0.0076	0.0001	-0.0370
Lymnaedae	0.00	0.0000	0.0000	0.0000
Planorbidae	0.00	0.0000	0.0000	0.0000
Helodidae	0.00	0.0000	0.0000	0.0000
Hydracarina	3.00	0.0076	0.0001	-0.0370
Psidium	0.00	0.0000	0.0000	0.0000
Limnophora	8.00	0.0202	0.0004	-0.0788
Σ	396.00		0.1069	-2.4943

Simpson's index, (1 / *D'*). *D'* = $\sum_{i=1}^{s} p_i^2$ **= 9.35**

Shannon-Weiner index, *H'* $= -\sum_{i=1}^{s} (P_i \ln p_i)$ **= 2.494**

Site D (species richness = 19) Spring 2003

	n	P*i*	P_i^2	P*i* ln*Pi*
Planaridae	0.00	0.0000	0.0000	0.0000
Oligochaeta	28.00	0.1489	0.0222	-0.2836
Glossiphonidae	1.00	0.0053	0.0000	-0.0279
Erpobdellidae	2.00	0.0106	0.0001	-0.0483
Gammaridae	72.00	0.3830	0.1467	-0.3676
Asellidae	0.00	0.0000	0.0000	0.0000
Heptagenidae	0.00	0.0000	0.0000	0.0000
Baetidae	14.00	0.0745	0.0055	-0.1934
Leuctridae	4.00	0.0213	0.0005	-0.0819
Taeniopterygidae	0.00	0.0000	0.0000	0.0000
Perlodidae	1.00	0.0053	0.0000	-0.0279
Chloroperlidae	0.00	0.0000	0.0000	0.0000
Nemouridae	1.00	0.0053	0.0000	-0.0279
Leptoceridae	0.00	0.0000	0.0000	0.0000
Lepidostomatidae	0.00	0.0000	0.0000	0.0000
Sericostomatidae	6.00	0.0319	0.0010	-0.1099
Glossosomatidae	1.00	0.0053	0.0000	-0.0279
Philopotamidae	0.00	0.0000	0.0000	0.0000
Odontoceridae	0.00	0.0000	0.0000	0.0000
Rhyacophilidae	0.00	0.0000	0.0000	0.0000
Polycentropodidae	1.00	0.0053	0.0000	-0.0279
Limnephilidae	3.00	0.0160	0.0003	-0.0660
Hydropsychidae	3.00	0.0160	0.0003	-0.0660
Dytiscidae	0.00	0.0000	0.0000	0.0000
Hygrobidae	2.00	0.0106	0.0001	-0.0483
Elmidae	0.00	0.0000	0.0000	0.0000
Tipulidae	1.00	0.0053	0.0000	-0.0279
Simulidae	3.00	0.0160	0.0003	-0.0660
Chironomidae	33.00	0.1755	0.0308	-0.3054
Ancylidae	0.00	0.0000	0.0000	0.0000
Sphaeridae	0.00	0.0000	0.0000	0.0000
Valvatidae	0.00	0.0000	0.0000	0.0000
Hydrobidae	0.00	0.0000	0.0000	0.0000
Lymnaedae	0.00	0.0000	0.0000	0.0000
Planorbidae	0.00	0.0000	0.0000	0.0000
Helodidae	0.00	0.0000	0.0000	0.0000
Hydracarina	1.00	0.0053	0.0000	-0.0279
Psidium	0.00	0.0000	0.0000	0.0000
Limnophora	11.00	0.0585	0.0034	-0.1661
$\sum$	188.00		0.2113	-1.9977

Simpson's index, (1 / *D*'). $D' = \sum_{i=1}^{s} p_i^2$ **= 4.73**

Shannon-Weiner index, $H' = -\sum_{i=1}^{s} (P_i \ln p_i)$ **= 1.998**

Site E (species richness = 16) Spring 2003

	n	P*i*	P_i^2	P*i* ln*P*i
Planaridae	25.00	0.0359	0.0013	-0.1194
Oligochaeta	84.00	0.1205	0.0145	-0.2550
Glossiphonidae	7.00	0.0100	0.0001	-0.0462
Erpobdellidae	30.00	0.0430	0.0019	-0.1354
Gammaridae	27.00	0.0387	0.0015	-0.1259
Asellidae	135.00	0.1937	0.0375	-0.3179
Heptagenidae	0.00	0.0000	0.0000	0.0000
Baetidae	273.00	0.3917	0.1534	-0.3671
Leuctridae	3.00	0.0043	0.0000	-0.0234
Taeniopterygidae	0.00	0.0000	0.0000	0.0000
Perlodidae	4.00	0.0057	0.0000	-0.0296
Chloroperlidae	0.00	0.0000	0.0000	0.0000
Nemouridae	0.00	0.0000	0.0000	0.0000
Leptoceridae	0.00	0.0000	0.0000	0.0000
Lepidostomatidae	0.00	0.0000	0.0000	0.0000
Sericostomatidae	5.00	0.0072	0.0001	-0.0354
Glossosomatidae	0.00	0.0000	0.0000	0.0000
Philopotamidae	0.00	0.0000	0.0000	0.0000
Odontoceridae	0.00	0.0000	0.0000	0.0000
Rhyacophilidae	2.00	0.0029	0.0000	-0.0168
Polycentropodidae	0.00	0.0000	0.0000	0.0000
Limnephilidae	0.00	0.0000	0.0000	0.0000
Hydropsychidae	56.00	0.0803	0.0065	-0.2026
Dytiscidae	0.00	0.0000	0.0000	0.0000
Hygrobidae	0.00	0.0000	0.0000	0.0000
Elmidae	0.00	0.0000	0.0000	0.0000
Tipulidae	1.00	0.0014	0.0000	-0.0094
Simulidae	13.00	0.0187	0.0003	-0.0743
Chironomidae	32.00	0.0459	0.0021	-0.1415
Ancylidae	0.00	0.0000	0.0000	0.0000
Sphaeridae	0.00	0.0000	0.0000	0.0000
Valvatidae	0.00	0.0000	0.0000	0.0000
Hydrobidae	0.00	0.0000	0.0000	0.0000
Lymnaedae	0.00	0.0000	0.0000	0.0000
Planorbidae	0.00	0.0000	0.0000	0.0000
Helodidae	0.00	0.0000	0.0000	0.0000
Hydracarina	0.00	0.0000	0.0000	0.0000
Psidium	0.00	0.0000	0.0000	0.0000
Limnophora	0.00	0.0000	0.0000	0.0000
Σ	697.00		0.2192	-1.8999

Simpson's index, (1 / *D*'). *D*' = $\sum_{i=1}^{s} p_i^2$ **= 4.56**

Shannon-Weiner index, *H*' = $-\sum_{i=1}^{s}(P_i \ln p_i)$ **= 1.9**

Site F (species richness = 12) Spring 2003

	n	P*i*	P_i^2	P*i* ln*Pi*
Planaridae	0.00	0.0000	0.0000	0.0000
Oligochaeta	79.00	0.1477	0.0218	-0.2825
Glossiphonidae	0.00	0.0000	0.0000	0.0000
Erpobdellidae	9.00	0.0168	0.0003	-0.0687
Gammaridae	8.00	0.0150	0.0002	-0.0628
Asellidae	136.00	0.2542	0.0646	-0.3482
Heptagenidae	0.00	0.0000	0.0000	0.0000
Baetidae	116.00	0.2168	0.0470	-0.3315
Leuctridae	0.00	0.0000	0.0000	0.0000
Taeniopterygidae	3.00	0.0056	0.0000	-0.0291
Perlodidae	0.00	0.0000	0.0000	0.0000
Chloroperlidae	0.00	0.0000	0.0000	0.0000
Nemouridae	0.00	0.0000	0.0000	0.0000
Leptoceridae	0.00	0.0000	0.0000	0.0000
Lepidostomatidae	0.00	0.0000	0.0000	0.0000
Sericostomatidae	8.00	0.0150	0.0002	-0.0628
Glossosomatidae	0.00	0.0000	0.0000	0.0000
Philopotamidae	0.00	0.0000	0.0000	0.0000
Odontoceridae	0.00	0.0000	0.0000	0.0000
Rhyacophilidae	3.00	0.0056	0.0000	-0.0291
Polycentropodidae	5.00	0.0093	0.0001	-0.0437
Limnephilidae	11.00	0.0206	0.0004	-0.0799
Hydropsychidae	54.00	0.1009	0.0102	-0.2315
Dytiscidae	0.00	0.0000	0.0000	0.0000
Hygrobidae	0.00	0.0000	0.0000	0.0000
Elmidae	0.00	0.0000	0.0000	0.0000
Tipulidae	0.00	0.0000	0.0000	0.0000
Simulidae	5.00	0.0093	0.0001	-0.0437
Chironomidae	97.00	0.1813	0.0329	-0.3096
Ancylidae	0.00	0.0000	0.0000	0.0000
Sphaeridae	0.00	0.0000	0.0000	0.0000
Valvatidae	0.00	0.0000	0.0000	0.0000
Hydrobidae	0.00	0.0000	0.0000	0.0000
Lymnaedae	0.00	0.0000	0.0000	0.0000
Planorbidae	0.00	0.0000	0.0000	0.0000
Helodidae	0.00	0.0000	0.0000	0.0000
Hydracarina	0.00	0.0000	0.0000	0.0000
Psidium	0.00	0.0000	0.0000	0.0000
Limnophora	1.00	0.0019	0.0000	0.0000
$\sum$	535.00		0.1779	-1.9141

Simpson's index, (1 / *D'*). *D'* = $\sum_{i=1}^{s} p_i^2$ **= 5.62**

Shannon-Weiner index, *H'* = $-\sum_{i=1}^{s} (P_i \ln p_i)$ **= 1.914**

Site G (species richness = 8) Spring 2003

	n	P*i*	P_i^2	P*i* ln*P*i
Planaridae	0.00	0.0000	0.0000	0.0000
Oligochaeta	169.00	0.2855	0.0815	-0.3579
Glossiphonidae	2.00	0.0034	0.0000	-0.0192
Erpobdellidae	13.00	0.0220	0.0005	-0.0839
Gammaridae	1.00	0.0017	0.0000	-0.0108
Asellidae	132.00	0.2230	0.0497	-0.3346
Heptagenidae	0.00	0.0000	0.0000	0.0000
Baetidae	191.00	0.3226	0.1041	-0.3650
Leuctridae	0.00	0.0000	0.0000	0.0000
Taeniopterygidae	0.00	0.0000	0.0000	0.0000
Perlodidae	0.00	0.0000	0.0000	0.0000
Chloroperlidae	0.00	0.0000	0.0000	0.0000
Nemouridae	0.00	0.0000	0.0000	0.0000
Leptoceridae	0.00	0.0000	0.0000	0.0000
Lepidostomatidae	0.00	0.0000	0.0000	0.0000
Sericostomatidae	0.00	0.0000	0.0000	0.0000
Glossosomatidae	0.00	0.0000	0.0000	0.0000
Philopotamidae	0.00	0.0000	0.0000	0.0000
Odontoceridae	0.00	0.0000	0.0000	0.0000
Rhyacophilidae	0.00	0.0000	0.0000	0.0000
Polycentropodidae	0.00	0.0000	0.0000	0.0000
Limnephilidae	0.00	0.0000	0.0000	0.0000
Hydropsychidae	0.00	0.0000	0.0000	0.0000
Dytiscidae	0.00	0.0000	0.0000	0.0000
Hygrobidae	0.00	0.0000	0.0000	0.0000
Elmidae	0.00	0.0000	0.0000	0.0000
Tipulidae	0.00	0.0000	0.0000	0.0000
Simulidae	31.00	0.0524	0.0027	-0.1545
Chironomidae	53.00	0.0895	0.0080	-0.2160
Ancylidae	0.00	0.0000	0.0000	0.0000
Sphaeridae	0.00	0.0000	0.0000	0.0000
Valvatidae	0.00	0.0000	0.0000	0.0000
Hydrobidae	0.00	0.0000	0.0000	0.0000
Lymnaedae	0.00	0.0000	0.0000	0.0000
Planorbidae	0.00	0.0000	0.0000	0.0000
Helodidae	0.00	0.0000	0.0000	0.0000
Hydracarina	0.00	0.0000	0.0000	0.0000
Psidium	0.00	0.0000	0.0000	0.0000
Limnophora	0.00	0.0000	0.0000	0.0000
$\sum$	592.00		0.2466	-1.5418

Simpson's index, (1 / *D'*). $D' = \sum_{i=1}^{s} p_i^2$ **= 4.06**

Shannon-Weiner index, $H' = -\sum_{i=1}^{s} (P_i \ln p_i)$ **= 1.542**

Site A (species richness = 27) Autumn 2003

	n	P*i*	P_i^2	-P*i* ln*P*i
Planaridae	9.00	0.0143	0.0002	-0.0606
Oligochaeta	131.00	0.2076	0.0431	-0.3264
Glossiphonidae	0.00	0.0000	0.0000	0.0000
Erpobdellidae	0.00	0.0000	0.0000	0.0000
Gammaridae	134.00	0.2124	0.0451	-0.3290
Asellidae	0.00	0.0000	0.0000	0.0000
Heptagenidae	24.00	0.0380	0.0014	-0.1243
Baetidae	20.00	0.0317	0.0010	-0.1094
Leuctridae	30.00	0.0475	0.0023	-0.1448
Taeniopterygidae	0.00	0.0000	0.0000	0.0000
Perlodidae	6.00	0.0095	0.0001	-0.0443
Chloroperlidae	0.00	0.0000	0.0000	0.0000
Nemouridae	32.00	0.0507	0.0026	-0.1512
Leptoceridae	0.00	0.0000	0.0000	0.0000
Lepidostomatidae	0.00	0.0000	0.0000	0.0000
Sericostomatidae	6.00	0.0095	0.0001	-0.0443
Glossosomatidae	0.00	0.0000	0.0000	0.0000
Philopotamidae	0.00	0.0000	0.0000	0.0000
Odontoceridae	1.00	0.0016	0.0000	-0.0102
Rhyacophilidae	5.00	0.0079	0.0001	-0.0383
Polycentropodidae	30.00	0.0475	0.0023	-0.1448
Limnephilidae	1.00	0.0016	0.0000	-0.0102
Hydropsychidae	14.00	0.0222	0.0005	-0.0845
Dytiscidae	1.00	0.0016	0.0000	-0.0102
Hygrobidae	0.00	0.0000	0.0000	0.0000
Elmidae	11.00	0.0174	0.0003	-0.0706
Tipulidae	7.00	0.0111	0.0001	-0.0499
Simulidae	49.00	0.0777	0.0060	-0.1984
Chironomidae	73.00	0.1157	0.0134	-0.2495
Ancylidae	2.00	0.0032	0.0000	-0.0182
Sphaeridae	0.00	0.0000	0.0000	0.0000
Valvatidae	0.00	0.0000	0.0000	0.0000
Hydrobidae	4.00	0.0063	0.0000	-0.0321
Lymnaedae	22.00	0.0349	0.0012	-0.1170
Planorbidae	0.00	0.0000	0.0000	0.0000
Velidae	1.00	0.0016	0.0000	-0.0102
Helodidae	12.00	0.0190	0.0004	-0.0754
Hydracarina	2.00	0.0032	0.0000	-0.0182
Psidium	2.00	0.0032	0.0000	-0.0182
Limnophora	2.00	0.0032	0.0000	-0.0182
$\sum$	631.00		0.1202	-2.5088

Simpson's index, (1 / *D*'). $D' = \sum_{i=1}^{s} p_i^2$ **= 8.31**

Shannon-Weiner index, $H' = -\sum_{i=1}^{s} (P_i \ln p_i)$ **= 2.51**

Site D (species richness = 12) Autumn 2003

	n	P*i*	P_i^2	-P*i* ln*P*i
Planaridae	0.00	0.0000	0.0000	0.0000
Oligochaeta	63.00	0.2647	0.0701	-0.3518
Glossiphonidae	0.00	0.0000	0.0000	0.0000
Erpobdellidae	0.00	0.0000	0.0000	0.0000
Gammaridae	24.00	0.1008	0.0102	-0.2313
Asellidae	0.00	0.0000	0.0000	0.0000
Heptagenidae	0.00	0.0000	0.0000	0.0000
Baetidae	1.00	0.0042	0.0000	-0.0230
Leuctridae	0.00	0.0000	0.0000	0.0000
Taeniopterygidae	0.00	0.0000	0.0000	0.0000
Perlodidae	1.00	0.0042	0.0000	-0.0230
Chloroperlidae	0.00	0.0000	0.0000	0.0000
Nemouridae	0.00	0.0000	0.0000	0.0000
Leptoceridae	0.00	0.0000	0.0000	0.0000
Lepidostomatidae	0.00	0.0000	0.0000	0.0000
Sericostomatidae	1.00	0.0042	0.0000	-0.0230
Glossosomatidae	0.00	0.0000	0.0000	0.0000
Philopotamidae	0.00	0.0000	0.0000	0.0000
Odontoceridae	0.00	0.0000	0.0000	0.0000
Rhyacophilidae	0.00	0.0000	0.0000	0.0000
Polycentropodidae	1.00	0.0042	0.0000	-0.0230
Limnephilidae	0.00	0.0000	0.0000	0.0000
Hydropsychidae	0.00	0.0000	0.0000	0.0000
Dytiscidae	0.00	0.0000	0.0000	0.0000
Hygrobidae	1.00	0.0042	0.0000	-0.0230
Elmidae	0.00	0.0000	0.0000	0.0000
Tipulidae	1.00	0.0042	0.0000	-0.0230
Simulidae	0.00	0.0000	0.0000	0.0000
Chironomidae	68.00	0.2857	0.0816	-0.3579
Ancylidae	0.00	0.0000	0.0000	0.0000
Sphaeridae	1.00	0.0042	0.0000	-0.0230
Valvatidae	0.00	0.0000	0.0000	0.0000
Hydrobidae	61.00	0.2563	0.0657	-0.3489
Lymnaedae	0.00	0.0000	0.0000	0.0000
Planorbidae	0.00	0.0000	0.0000	0.0000
Velidae	0.00	0.0000	0.0000	0.0000
Helodidae	0.00	0.0000	0.0000	0.0000
Hydracarina	15.00	0.0630	0.0040	-0.1742
Psidium	0.00	0.0000	0.0000	0.0000
Limnophora	0.00	0.0000	0.0000	0.0000
$\sum$	238.00		0.2317	-1.6252

Simpson's index, (1 / *D*'). $D' = \sum_{i=1}^{s} p_i^2$ **= 4.32**

Shannon-Weiner index, $H' = -\sum_{i=1}^{s} (P_i \ln p_i)$ **= 1.625**

Site E (species richness = 14) Autumn 2003

	n	P*i*	P_i^2	-P*i* ln*P*i
Planaridae	32.00	0.0215	0.0005	-0.0825
Oligochaeta	96.00	0.0645	0.0042	-0.1768
Glossiphonidae	17.00	0.0114	0.0001	-0.0511
Erpobdellidae	90.00	0.0604	0.0037	-0.1696
Gammaridae	158.00	0.1061	0.0113	-0.2380
Asellidae	727.00	0.4882	0.2384	-0.3500
Heptagenidae	0.00	0.0000	0.0000	0.0000
Baetidae	3.00	0.0020	0.0000	-0.0125
Leuctridae	0.00	0.0000	0.0000	0.0000
Taeniopterygidae	0.00	0.0000	0.0000	0.0000
Perlodidae	0.00	0.0000	0.0000	0.0000
Chloroperlidae	0.00	0.0000	0.0000	0.0000
Nemouridae	0.00	0.0000	0.0000	0.0000
Leptoceridae	0.00	0.0000	0.0000	0.0000
Lepidostomatidae	0.00	0.0000	0.0000	0.0000
Sericostomatidae	10.00	0.0067	0.0000	-0.0336
Glossosomatidae	0.00	0.0000	0.0000	0.0000
Philopotamidae	0.00	0.0000	0.0000	0.0000
Odontoceridae	0.00	0.0000	0.0000	0.0000
Rhyacophilidae	0.00	0.0000	0.0000	0.0000
Polycentropodidae	0.00	0.0000	0.0000	0.0000
Limnephilidae	0.00	0.0000	0.0000	0.0000
Hydropsychidae	334.00	0.2243	0.0503	-0.3353
Dytiscidae	0.00	0.0000	0.0000	0.0000
Hygrobidae	0.00	0.0000	0.0000	0.0000
Elmidae	0.00	0.0000	0.0000	0.0000
Tipulidae	0.00	0.0000	0.0000	0.0000
Simulidae	0.00	0.0000	0.0000	0.0000
Chironomidae	4.00	0.0027	0.0000	-0.0159
Ancylidae	0.00	0.0000	0.0000	0.0000
Sphaeridae	0.00	0.0000	0.0000	0.0000
Valvatidae	1.00	0.0007	0.0000	-0.0049
Hydrobidae	0.00	0.0000	0.0000	0.0000
Lymnaedae	0.00	0.0000	0.0000	0.0000
Planorbidae	1.00	0.0007	0.0000	-0.0049
Velidae	0.00	0.0000	0.0000	0.0000
Helodidae	0.00	0.0000	0.0000	0.0000
Hydracarina	0.00	0.0000	0.0000	0.0000
Psidium	14.00	0.0094	0.0001	-0.0439
Limnophora	2.00	0.0013	0.0000	-0.0089
Σ	1489.00		0.3085	-1.5279

Simpson's index, (1 / *D*'). *D*' = $\sum_{i=1}^{s} p_i^2$ **= 3.24**

Shannon-Weiner index, *H*' = $-\sum_{i=1}^{s} (P_i \ln p_i)$ **= 1.528**

Site F (species richness = 14) Autumn 2003

	n	P*i*	P_i^2	-P*i* ln*P*i
Planaridae	0.00	0.0000	0.0000	0.0000
Oligochaeta	48.00	0.0463	0.0021	-0.1423
Glossiphonidae	0.00	0.0000	0.0000	0.0000
Erpobdellidae	3.00	0.0029	0.0000	-0.0169
Gammaridae	16.00	0.0154	0.0002	-0.0644
Asellidae	827.00	0.7983	0.6372	-0.1799
Heptagenidae	0.00	0.0000	0.0000	0.0000
Baetidae	14.00	0.0135	0.0002	-0.0582
Leuctridae	0.00	0.0000	0.0000	0.0000
Taeniopterygidae	0.00	0.0000	0.0000	0.0000
Perlodidae	0.00	0.0000	0.0000	0.0000
Chloroperlidae	0.00	0.0000	0.0000	0.0000
Nemouridae	0.00	0.0000	0.0000	0.0000
Leptoceridae	0.00	0.0000	0.0000	0.0000
Lepidostomatidae	0.00	0.0000	0.0000	0.0000
Sericostomatidae	6.00	0.0058	0.0000	-0.0298
Glossosomatidae	0.00	0.0000	0.0000	0.0000
Philopotamidae	0.00	0.0000	0.0000	0.0000
Odontoceridae	0.00	0.0000	0.0000	0.0000
Rhyacophilidae	0.00	0.0000	0.0000	0.0000
Polycentropodidae	7.00	0.0068	0.0000	-0.0338
Limnephilidae	3.00	0.0029	0.0000	-0.0169
Hydropsychidae	50.00	0.0483	0.0023	-0.1463
Dytiscidae	0.00	0.0000	0.0000	0.0000
Hygrobidae	0.00	0.0000	0.0000	0.0000
Elmidae	0.00	0.0000	0.0000	0.0000
Tipulidae	0.00	0.0000	0.0000	0.0000
Simulidae	0.00	0.0000	0.0000	0.0000
Chironomidae	46.00	0.0444	0.0020	-0.1383
Ancylidae	0.00	0.0000	0.0000	0.0000
Sphaeridae	0.00	0.0000	0.0000	0.0000
Valvatidae	0.00	0.0000	0.0000	0.0000
Hydrobidae	0.00	0.0000	0.0000	0.0000
Lymnaedae	2.00	0.0019	0.0000	-0.0121
Planorbidae	0.00	0.0000	0.0000	0.0000
Velidae	0.00	0.0000	0.0000	0.0000
Helodidae	0.00	0.0000	0.0000	0.0000
Hydracarina	1.00	0.0010	0.0000	-0.0067
Psidium	12.00	0.0116	0.0001	-0.0516
Limnophora	1.00	0.0010	0.0000	-0.0067
$\sum$	1036.00		0.6443	-0.9039

Simpson's index, (1 / *D*'). $D' = \sum_{i=1}^{s} p_i^2$ **= 1.55**

Shannon-Weiner index, $H' = -\sum_{i=1}^{s} (P_i \ln p_i)$ **= 0.904**

Site G (species richness = 13) Autumn 2003

	n	P*i*	P_i^2	-P*i* ln*P*i
Planaridae	0.00	0.0000	0.0000	0.0000
Oligochaeta	30.00	0.0615	0.0038	-0.1715
Glossiphonidae	3.00	0.0061	0.0000	-0.0313
Erpobdellidae	3.00	0.0061	0.0000	-0.0313
Gammaridae	8.00	0.0164	0.0003	-0.0674
Asellidae	373.00	0.7643	0.5842	-0.2054
Heptagenidae	0.00	0.0000	0.0000	0.0000
Baetidae	8.00	0.0164	0.0003	-0.0674
Leuctridae	0.00	0.0000	0.0000	0.0000
Taeniopterygidae	0.00	0.0000	0.0000	0.0000
Perlodidae	0.00	0.0000	0.0000	0.0000
Chloroperlidae	0.00	0.0000	0.0000	0.0000
Nemouridae	0.00	0.0000	0.0000	0.0000
Leptoceridae	0.00	0.0000	0.0000	0.0000
Lepidostomatidae	0.00	0.0000	0.0000	0.0000
Sericostomatidae	0.00	0.0000	0.0000	0.0000
Glossosomatidae	0.00	0.0000	0.0000	0.0000
Philopotamidae	0.00	0.0000	0.0000	0.0000
Odontoceridae	0.00	0.0000	0.0000	0.0000
Rhyacophilidae	0.00	0.0000	0.0000	0.0000
Polycentropodidae	0.00	0.0000	0.0000	0.0000
Limnephilidae	1.00	0.0020	0.0000	0.0000
Hydropsychidae	0.00	0.0000	0.0000	0.0000
Dytiscidae	0.00	0.0000	0.0000	0.0000
Hygrobidae	0.00	0.0000	0.0000	0.0000
Elmidae	0.00	0.0000	0.0000	0.0000
Tipulidae	0.00	0.0000	0.0000	0.0000
Simulidae	0.00	0.0000	0.0000	0.0000
Chironomidae	11.00	0.0225	0.0005	-0.0855
Ancylidae	0.00	0.0000	0.0000	0.0000
Sphaeridae	0.00	0.0000	0.0000	0.0000
Valvatidae	0.00	0.0000	0.0000	0.0000
Hydrobidae	3.00	0.0061	0.0000	0.0000
Lymnaedae	11.00	0.0225	0.0005	0.0000
Planorbidae	0.00	0.0000	0.0000	0.0000
Velidae	0.00	0.0000	0.0000	0.0000
Helodidae	1.00	0.0020	0.0000	0.0000
Hydracarina	1.00	0.0020	0.0000	0.0000
Psidium	32.00	0.0656	0.0043	0.0000
Limnophora	3.00	0.0061	0.0000	0.0000
$\sum$	488.00		0.5940	-0.6597

Simpson's index, (1 / *D'*) . *D'* = $\sum_{i=1}^{s} p_i^2$ **= 1.68**

Shannon-Weiner index, *H'* = $-\sum_{i=1}^{s} (P_i \ln p_i)$ **= 0.66**

Site	Ag	Al	Be	Cd	Cr	Cu	Fe	Pb	Mn	Na	Ni	Zn	Tot
a	3.4	3841	0.032	0.27	11.6	3.9	17517	14.9	592	1100.8	8.9	26.7	23143
d	4.45	4086	0.36	0.86	284	22.4	22459	38.6	299.1	1093.1	10.7	27.7	28356.87
e	4.93	3390	0.39	0.64	21.7	6.3	27092	19.5	242.3	1242	7.4	28.4	32101.96
f	9.53	4820	0.36	0.56	17.6	15	21050	30.8	1242	800.5	12.5	44.2	28072.85
g	4.92	4216	0.24	0.48	72.2	17.7	12517	50.3	915	971.6	10.9	49.3	18850.14

Mean concentrations of sediment metals: all values in mg kg^{-1}

PAH	Site a	Site d	Site e	Site f	Site g
Naphthalene	51.904	8.851	79.570	29.262	43.054
Acenaphthylene	3.082	29.331	9.423	3.452	26.037
Acenaphthene	3.608	116.001	35.789	8.622	181.445
Fluorene	8.576	134.489	27.627	14.430	210.762
Anthracene	1023.205	2013.459	635.496	601.564	1353.580
Phenanthrene	251.189	1784.683	144.170	219.490	3812.165
Fluoranthene	516.318	2690.556	0.000	292.243	5591.952
Pyrene	537.330	2242.143	754.672	278.784	4725.601
Benz[a]anthracene	148.027	754.815	0.000	0.000	2482.834
Chrysene	342.355	991.801	0.000	371.287	2425.609
Benzo[b]fluoranthene	0.000	1012.391	905.114	709.474	1649.552
Benzo[k]fluoranthene	917.015	1029.061	0.000	744.527	1843.315
Benzo[g,h,I]perylene	662.916	645.742	0.000	0.000	1614.654
Indeno[1,2,3-cd]perylene	375.192	961.770	0.000	0.000	0.000
Dibenz[a,h]anthracene	694.460	831.799	0.000	0.000	0.000
Total PAHs	5535.176	15246.893	2591.862	3273.135	25960.561

Mean PAH concentrations: all values in μg kg^{-1}. Values below the limit of detection were entered as zero values.

Appendix IX

Hazard Ranking Score Categories

Class 1: Action Required

The available information indicates that action (e.g., mitigation or elimination of contaminant sources, risk management, or remediation) is needed to address existing sediment quality concerns. Typically, Class 1 sites will have widespread and high levels of sediment contamination, and measured or observed impacts on species composition/diversity and tissue burden will have been documented.

Class 2: Action Likely Required

The available information indicates there is a moderate to high potential for adverse biological effects and action (such as those described for Class 1 sites) will likely be necessary to address the sediment quality concerns. Class 2 sites will typically be those with localised areas of moderate to high contamination. Impacts to biological components are indicated, but may not have been assessed.

Class 3: Action May be Required

The available information indicates there is a low to moderate potential for adverse biological effects and action may be necessary to address the sediment quality concerns. Class 3 sites will typically be those with localised areas of low to moderate contamination. Additional sediment and biological assessments may be carried out to affirm the site classification and identify requirements for further action.

Class N: Action Not Likely Required

The available information indicates there is likely no significant environmental concerns related to sediment quality. There is no indicated need for action unless new information indicates a higher level of concern. In that case, a re-assessment of the site is warranted.

Class I: Insufficient Information

There is insufficient information to classify the site, and a comprehensive sediment assessment is required to address data gaps.

Appendix X

Raingauge and laboratory equipment calibration

Raingauges

The manufacturers claim an accuracy of 97% for rainfalls up to 100 mm/hr but up to 99% for rainfalls up to 90 mm/hr. More important however, are the reported inaccuracies associated with siting raingauges in an elevated position. Advice was sought from the Met Office who suggested placing a daily raingauge within the catchment. As a resolution greater than that provided by daily totals is required, readings from this type of gauge would be useful in calculating the percentage error associated with the elevated tipping buckets. In order to measure the accuracy of the Potter Hill tipping-bucket raingauge, a 'Snowdon' type 8" Met Office approved raingauge was emplaced (also conforming to Met Office installation guidelines) at the site. Installation took place on the 13th February 2003 and collected rainfall was measured daily until the 3rd April 2003. Rainfall was captured on 20 days out of the 50 days calibration period. The original intention was to measure for a period of one month; however, February proved to be the driest since 1998 and March only produced 54% of the 1961 - 1990 average rainfall for that month (BBC, 2003).
Comparison of the tipping-bucket recorded values and daily raingauge measurements show a close correlation. Errors were greater for lower rainfall measurements (< 1.0 mm). This was felt to be due to the tipping-bucket recording in whole tips of 0.2 mm, leading to a potential inaccuracy of 0.4 mm for any given day. In contrast, the daily monitoring was able to record fractions of the tipping bucket load. Over the period of the calibration exercise, the daily rainfall measurements totalled 48.6 mm compared to 50 mm for the tipping-bucket. The results obtained provided a sufficient degree of accuracy for future reliance on the tipping-buckets alone. Further calibration was carried out in the Autumn of 2003 to confirm the accuracy of the gauge.
The school raingauge calibration was carried out using a Watson-Marlow peristaltic pump, Model 502-S. Initial calibration of the pump was carried out in the laboratory with discharge rates calculated for a range of tube bores.

Volumes of water were discharged using all three bores for measured time intervals at each raingauge. Pump discharge rates, when related to the raingauges in use [203 mm ∅], equated to rainfall intensities of 114.6 mm / hr $^{-1}$, 62.6 mm / hr $^{-1}$ and 7.9 mm / hr $^{-1}$ respectively.
Repeat calibration was carried out on site, with water discharged to the raingauge at different pipe bores to mimic different intensities and the recorded tips compared to known discharge. Differences were noted in the field, with the peristaltic pump discharging slightly greater volumes than that recorded in the laboratory. It was noted that there was increasing accuracy with greater bore size (see table 1).

Tube bore ∅	Q Laboratory (mm / min)	Q Site (mm / min)	% Difference
1.8	4.24	4.65	9
3.3	33.75	35.25	4
4.8	61.83	61.9	1

Table 1: Peristaltic pump calibration data.

The raingauge performed well with a total recorded 'rainfall' of 15.8 mm over the calibration period from an introduced discharge of 15.3 mm, equating to an overall error of 3 %.
One raingauge utilised a 'Newlog' universal data-logging module whose data is downloaded via a 'Husky Hunter' data retriever. The other raingauge utilised a 'Rainlog' data logger, which downloads direct to a PC. The data retrievers were synchronised with each other, with the internal clock of the PC used to set up the loggers following each download. Maintenance of synchronicity was carried out fortnightly to counteract potential drift. Data was downloaded at the same frequency.

Laboratory and metering equipment

DO The probe was calibrated on-site at measuring temperature to increase accuracy at the same frequency as the sampling regime, using the water saturated air method as per the manfacturers recommendations.
pH Both meters were calibrated using Merck CertiPUR buffers of pH 4, 7 & 10.
Ammonia calibration was per the manufacturers recommendations using standard stock solutions of 1 mg / ml and 10 g / ml to prepare ammonia concentrations of 0.1, 1.0, 5.0 and 10 mg / l.
COD heating block calibration was carried out using a wide range thermometer (0 - 300^{0}C), placed in a glycerine filled digestion tube. This allowed adjustments to be made if required throughout the digestion process.
The BOD incubator was calibrated to the specified temperature of 20 ^{0}C ± 0.5 ^{0}C (SCA, 1981), by filling glass bottles with water and placing one in each corner of each shelf and checking the temperature every 24 hours, by thermometer. The thermostat was adjusted until the required temperature was achieved for all bottles at which point the thermostat temperature was noted. Thereafter, temperature was monitored continuously using a thermometer placed in a water-filled BOD bottle placed centrally within the incubator, with adjustments to the thermostat made as required.

The table below gives a summary of all the analyses and methods used in this phase of the study.

Analysis	Method
Ammonia	SCA (1981)
Biochemical Oxygen Demand	SCA (1988)
Chemical Oxygen Demand	SCA (1986)
Hardness	SCA (1982)
pH	SCA (1988)
Suspended sediment	SCA (1980)
Temperature	SCA (1987)

Instrument	Calibration method (reference)
Ammonia meter	SCA (1981)
DO probe	Water saturated air
Heating block	Electronic thermometer
Oven	Wide range thermometer in glycerine
Incubator	SCA (1988)
pH probe	Merck CertiPUR buffers at pH 4, 7 & 10

Appendix XI

Draft of paper to be submitted for publication in *The Science of the Total Environment*

Stream quality in a small urbanised catchment

Matthew Robson [a], Kevin Spence [a] *Lindsey Beech [b],

[a] *Sheffield Hallam University, Howard Street, Sheffield, South Yorkshire, S1 1WB, UK.*
[b] *17, Royal Crescent, Bath, Somerset, BA1 2LT, UK.*

Abstract

River-length patterns in the chemistry and biology of the Charlton Brook, an unclassified watercourse in northwest Sheffield have been examined. Five sampling sites for macroinvertebrates and pollutant analysis were used, in conjunction with Environment Agency General Quality Assessment (GQA) methodologies and hydraulic analysis of the catchment. Sites were strategically located to account for the tributaries and the brook downstream of their confluence, to assess the potential impact from surface water outfalls (SWOs).

Variations in GQA parameters indicate a significant drop in quality downstream of the SWOs that discharge to the study watercourse, with a marked drop in biological diversity noted at the onset of urbanisation. The decline in biological quality however is greater than that suggested by physico-chemical analysis alone. There was a significant inverse relationship between impermeable area and biological diversity.

Analysis of polycyclic aromatic hydrocarbons (PAHs) and trace metals in sediment from the watercourse showed significant, yet irregular between site variations.

The potential toxicity of instream metal concentrations was determined using cumulative criterion unit (CCU) scores. CCU analysis highlighted cadmium, copper and lead as the major sources of potential instream toxicity with all sites exceeding the threshold for likely harm to aquatic life.

In the absence of different physical characteristics, comparisons of the chemical and biological data indicate that the benthic macroinvertebrate

*corresponding author. Tel.: 0114-2254722; Fax: 0114-2253206.
E-mail address: k.j.spence@shu.ac.uk (K. Spence)

population of such watercourses are adversely affected by the stormwater inputs.

Keywords: Macroinvertebrates; Stormwater; Unclassified rivers; CCU; Water quality.

1. Introduction

The total river length in England & Wales is estimated to be between 95,000 and 130,000 km (Furse, 1997), the majority of which do not receive classification and therefore are not subject to the routine Environment Agency General Quality Assessments (GQA). However, one of the principal environmental objectives of the EC Water Framework Directive; Article 4, is to ensure achievement and maintenance of 'good status' for all Community waters by 2015 (2000/60/EC); rather than "those that member states choose to designate" (DETR, 2001). The proportion of these unclassified watercourses receiving discharges from urbanised catchments is unknown, however due to housing growth, it is estimated that the urban area of England alone will increase from the 10.6% existing in 1991 to 11.9% by 2016 (Housebuilders Federation, 2002). Although the Review of the Building Regulations, 1991 (Part H), encourages the use of sustainable urban drainage systems, use of SWOs may still occur depending on site conditions, resulting in a further deterioration of in-stream quality, without widening statutory control.

It is documented that contaminants transported within stormwater discharges from urbanised catchments are a major cause of impairment to receiving waters, (Myers et al., 1985; USEPA, 1990; Makepeace, et al., 1995; Novotny, 1995; Environment Agency, 1998). Typical determinants include total suspended solids BOD, COD, heavy metals, hydrocarbons and bacteria of animal origin, (Hvitved-Jacobsen & Yousef, 1991). It is suggested that although biochemical stormwater pollutant concentrations are generally less than those for combined sewer overflows (CSOs), they do discharge a greater volume of water on an annual basis (Ellis & Hvitved-Jacobsen, 1996), and hence a greater mass of pollutants

Unlike CSOs, stormwater discharges from separately sewered catchments are not routinely regulated in the UK. Despite this, contamination of surface waters is unlikely to decrease, with vehicular induced pollution likely to increase as traffic volumes are forecast to grow from 488 billion vehicle km in 2000 to 688 billion vehicle km a year in 2025 in the UK (Transport Research Laboratory, 2002).

Although the effects of stormwater associated with CSO discharges and highway runoff have been widely studied (Seager & Abrahams, 1990; Maltby et al., 1995; Wagner & Geiger, 1996; Perdikaki & Mason, 1999; Sriyaraj & Shutes, 2001), few investigations have concentrated on surface water outfalls in isolation and their biological and chemical impact on unclassified rivers; that is, watercourses with an average summer flow of less than 0.3 m^3 s^{-1} (Robins, 2001).

Payne (1989), in her study of 47 individual surface water sewers, came to the broad conclusion that biological diversity decreases with increasing area of sewered catchment and that impacts are more likely to occur downstream of outfalls fed by catchments over 50 hectares, with residential areas having the least impact. Payne suggested that the greatest score reductions occur where the initial water quality is highest. However, no attempt was made to measure the quantity or quality of discharges or the cumulative impact of successive outfalls on a sub-catchment level.

The mean annual concentration of pollutants from stormwater discharges has been compared to sewage following secondary treatment (Hvitved-Jacobsen, 1986). Yet during storm events, peak concentrations can be much higher than treatment plant discharges. Saget et al., (1998) calculated that the maximum load that could be generated by a rainfall event could reach four and seven times that from a treatment plant for BOD and COD respectively and that for suspended solids, the maximum load generated by a rain event may be as much as 26 times the dry weather load from a treatment plant. These impacts would, it is argued, be even worse if applied to other pollutants such as heavy metals and hydrocarbons due to their greater concentration in runoff than industrial and domestic sewage (Saget et al., ibid.). Sediments act as both sinks and sources of pollutants, and are indicated as the cause of beneficial use impairments (Burton & Pitt, 2002). The accumulation of contaminated

streambed sediments is argued to be the principle underlying reason for reduced biointegrity (Beasley & Kneale, 2002). Consequently, sediments were targeted as potential problem sources during this study with sediments from the brook sampled and analysed for metals and polycyclic aromatic hydrocarbons (PAHs).

Work by others has indicated an additive chronic toxicity of metal mixtures in natural waters (Enserink et al., 1991) leading to development of the cumulative criterion unit (CCU; Clements et al., 2000), a recently defined measure of total metal concentration and toxicity. It is calculated for any site based on the U.S. Environmental Protection Agency criterion continuous concentration (CCC) values for toxicity (USEPA, 1986). Its instrumentality lies in expressing the additive effects of each metal relative to postulated toxic thresholds as a single variable. The CCU is with one exception (Hirst et al., 2002), untested in the UK. This study incorporated the measure to assess whether CCUs could indicate metal toxicity in relation to macroinvertebrate assemblages. Derived metal concentrations were used to calculate CCU scores thus:

$$\mathrm{CCU} = \sum_{i=1}^{n} mi / ci$$

where m_i is the total recoverable metal concentration and c_i is the hardness-adjusted CCC value for the *i*th metal. For Al, Fe and Mn the authors have followed the EPA chronic criterion values of 87, 1000 and 1000 μg / L^{-1}, respectively. Due to the effects of water hardness on the toxicity and bioavailability of certain heavy metals, criterion values for Ag, Cd, Cr, Cu, Pb, Ni and Zn are modified to take this into account (U.S. EPA, 1986; 1999; 2002). Metals below the level of detection are not included in the CCU.

Sediment quality guidelines, incorporating both metals and PAHs, based on the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (CCME, 1995), can be utilised to rank samples in a manner similar to that for deriving CCU scores. The method is based on Long and MacDonald's (1997) PEL quotient approach, using sites' mean PEL (Probable

Effects Level) quotients and/or number of PELs exceeded to determine relative site priorities. The normalised PEL-quotient is derived thus:

$$\text{Normalised PEL-Quotient} = \frac{\sum \frac{m}{p}}{q}$$

Where m is the measured contaminant concentration, p is the probable effect level and q is the number of PEL-quotients calculated. Pollutant levels below the limit of detection were not included. The two endpoints (the normalised PEL-quotient and the number of guidelines exceeded) then serve to prioritise sites of concern (CSMWG, 2003).

2. Study aims

The purpose of the study was to;

1. Examine the spatial variation of freshwater macroinvertebrate communities in the study catchment.
2. Investigate the potential cause of any impairment through determination of the organic and inorganic chemical characteristics of the watercourse.

3. Methods

3.1. Study site

The study catchment comprises Charlton Brook and its tributaries which rises in Wharncliffe chase. This is a partially urbanised tributary of the Blackburn Brook in northeast Sheffield that has a catchment area of 374 hectares. The brook flows eastwards from its origin at an altitude of 230 m, joining the Blackburn Brook in Chapeltown (Ordnance Survey National Grid Reference SK 3538 9689) at an altitude of 95 m. The channel slope is 36.4 m km^{-1} determined as the average slope between two points located 10

and 85 % along the mainstream length of 3.7 km (Hall et al., 1993). The upstream portion of the catchment, comprising three main tributaries is predominantly rural, consisting of agricultural grassland and deciduous woodland. Downstream of their confluence, the catchment is almost entirely urbanised. The urban portion of the brook is bordered by woodland and amenity grassland and has been identified as a key site and strategic green link in the South Yorkshire Forest Plan (South Yorkshire Forest Partnership, 1998). The catchment is separately sewered and all discharges to the brook are in the form of SWOs, sixteen in all, which are located in the urban portion of the catchment (see Figure 1)

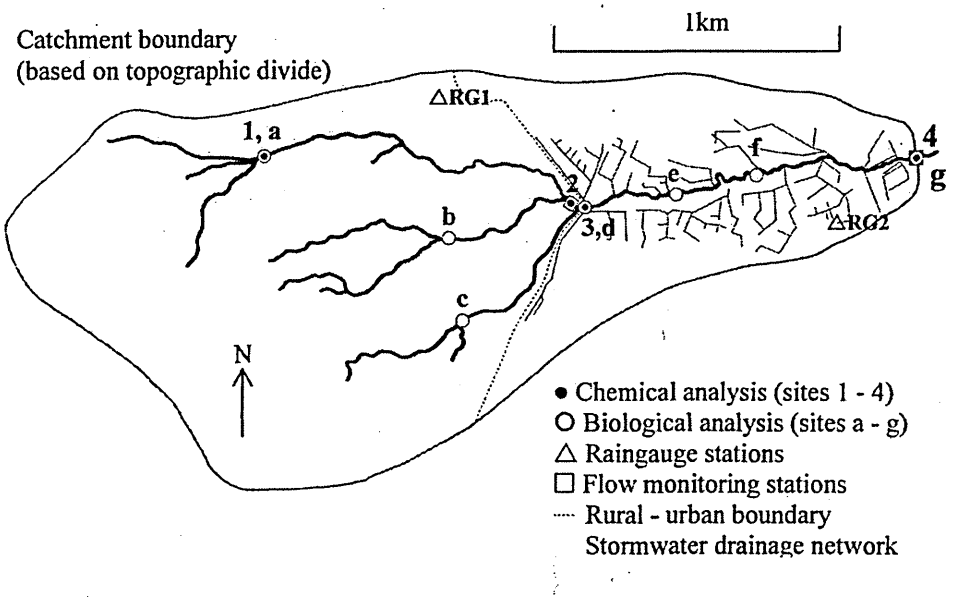


Fig. 1: River and drainage networks, showing biological and chemical sampling points, Charlton Brook.

There was evidence of a small quantity of sewer litter from a single outfall, approximately midway between sites e and f, suggesting some misconnection of foul drainage to the surface water drainage system. This misuse has been reported elsewhere (Payne, 1989). The urbanised proportion of the catchment is 24.7%, comprising medium density housing including two schools; with commercial premises limited to a corner shop, garage and two public houses. The drainage network covers 14.5 % of the catchment with a

total impermeable area of 20.09 hectares. The impermeability of this urban area was calculated from an average of ten representative $100m^2$ grids. The remaining urban area does not contribute to the stormwater network.

3.2. Sample collection and preparation

Benthic macroinvertebrate samples were obtained from each of the three tributaries and from a series of locations along the brook itself (Figure 1). Sampling was carried out during low-flow conditions in May and September 2003. All sampling sites were chosen to be similar with respect to light and shade, substrate type, velocity (< 0.4 m / s), flow depth (5 - 6 cm) and channel width (2 - 3 m). This was to increase the likelihood that observed differences could be attributable to the SWOs rather than riverine characteristics. The macroinvertebrates were collected by 3-minute kick sample and 1-minute manual search using a square headed pond net, mesh size 900 μm, with all samples collected from riffles (Mason, 2002), this being the recognised standard method employed by the Environment Agency (2003). In the laboratory, the macroinvertebrates were separated from the substrate and preserved in 70 % ethanol for later identification to family level.

Samples for biochemical analysis were collected in polypropylene containers from points located at the upstream rural, downstream rural, upstream urban and downstream urban portions of the catchment (Figure 1). Water samples (2 L) were taken for chemical analysis on a fortnightly basis between January 2002 and September 2003 to give a sufficient quantity of data during the study period. Interrogation of the flow monitoring equipment confirmed that the watercourse was experiencing baseflow during the regular sampling activity. Additionally, samples for CCU determination were collected in January and June, 2004, to see if there was a seasonal variation in scores.

Multiple samples of sediment (approx 1 kg in total) were collected randomly at each site from the top 5 cm of sediment, using a trowel and in sequence from downstream to upstream. This method produces minimal disturbance of the streambed, low risk of contamination and minimal loss of

the finest particles that generally possess the highest metal concentrations (Beasley & Kneale, 2003).

Each composite sample was stored in high-density polyethylene containers for metal analysis. The process was repeated with samples stored in amber glass jars for PAH analysis. Sediment was prepared for metal analysis by coning and quartering the dried sediment, of which 0.2 g was placed into acid-washed glass test tubes into which 10 ml of Aristar nitric acid was added. The tubes were placed in a preheated Grant™ block digester at 80^0C for 2 hours. On cooling, the samples are transferred to acid-washed volumetric flasks and made up to 50 ml with distilled water. The technique used to extract polycyclic aromatic hydrocarbons from the sediment samples followed the U.S. Environmental Protection Agency's Method 3540C (U.S. EPA, 1996) with extracts concentrated to 1 ml, prior to analysis for hydrocarbons. Cleanup procedure followed that of the U.S. EPA Method 610 (U.S. EPA, 2003).

3.3. Analytical procedures

Macroinvertebrates were sorted and identified to family level using standard keys. Macroinvertebrate abundance was recorded and the data used to calculate diversity, richness and evenness indices. Species richness, or number of taxa, is the simplest measure of biodiversity within a sample. Calculation of ASPT, which is independent of sample size, is a quick and straightforward scoring system regarded as a stable and reliable index of organic pollution (Environment Agency, 2003). Indices based on sensitivity to organic pollution alone however, were considered insufficient in ascribing the potential effect of pollution that includes contaminants more specific to stormwater such as trace metals. Consequently the Shannon-Weiner diversity index and Pielou's evenness index were additionally employed in analysis of the biological data.

Water samples were analysed for DO, BOD_5, COD, ammonia, suspended solids, hardness and temperature. All biochemical analyses were carried out on the day of sampling, with BOD samples brought to incubation temperature within 6 hours of sampling. BOD, COD, ammonia and suspended

solids determination was carried out in accordance with the Standing Committee of Analysts (SCA, 1986; 1988; 1981; 1980). Hand-held meters were used to measure pH, dissolved oxygen and temperature in the field. Organic pollution was determined using the method employed by the EA for their chemical GQA.

Metals were analysed using a Hewlitt Packard Spectroflame Model-P Optical Emission Spectrometer. The metals determined in these analyses were Ag, Al, Be, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn.

Sediment extracts were analysed for 15 selected PAHs: naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, indeno[1,2,3-cd]perylene and dibenz[a,h]anthracene. These PAHs are determined by the Scottish Environmental Protection Agency for their Diffuse Pollution Initiative (Wilson, 2003) which contains the 13 PAHs listed by Burton & Pitt (2002), for which reliable USEPA sediment quality guidelines are available. PAH analysis was carried out via positive electron ionisation using a Hewlett Packard 5890-A gas chromatograph. Calibration was achieved using a RESTEK™ SV Calibration Mix (2000 µl / ml in methylene chloride), at concentrations of 1, 12.5, 25 and 50 µl / ml. An internal standard of 25 µl / ml was introduced to each sample using a RESTEK™ Anthracene D 10 Mix.

3.4. Hydrometric data collection

Stream velocity, stage and discharge have been continuously monitored at the downstream end of the catchment (site 4, Figure 1) with a STARFLOW™ ultrasonic doppler instrument. Sampling frequency was set at 60-second intervals with an aggregate logging frequency of every five minutes. STARFLOW measurements were calibrated using laboratory flumes prior to installation. Due to limitations with the STARFLOW in accurate measurement of low velocities, discharge values were derived using a Mariotte vessel to dilution gauge the watercourse. Data were also collected from the watercourse at the rural / urban boundary, below site 2 (Figure 1) using a rectangular thin-

plate weir, primarily to verify modelled simulations of storm events. Rainfall has been continuously measured at two sites within the catchment using tipping bucket raingauges utilising integral data loggers. The rain gauge at site RG1 was accompanied by a 'Snowdon' daily raingauge for calibration purposes.

3.5 Statistical methods

Statistical methods used in the determination of GQA grade follow that employed by the Environment Agency, (2003). The relationship between macroinvertebrate species richness, diversity and evenness, individual family abundance, individual metals and CCUs were assessed using Pearson's correlations. Hydrocarbon and metal concentrations were analysed using two-sample *t* tests. All analyses were performed using the MINITAB statistical package (MINITAB, 1991). All values were assessed at the $p < 0.05$ significance level. Diversity indices were calculated using standard formulae (Ludwig & Reynolds, 1988).

4. Results

4.1. Physico-chemical

Dissolved oxygen decreased and biochemical oxygen demand increased from the upstream rural to the downstream urban areas, with significant differences in values between site 1 and site 4 (Table 1). Derived GQA grades also indicate a general decline in water quality, with BOD, DO and ammonia all dropping two grades over the length of the watercourse. This analysis of the regular sampling data confirms that there was a deterioration in chemical quality below the surface water outfalls.

Parameter	Result	Site 1	Site 2	Site 3	Site 4
BOD (mg / l)	Mean	1.315	1.560	2.245	2.915
	SD	0.647	0.830	0.937	1.350
	90 percentile	2.24	2.84	3.46	5.07
	Grade	**A**	**B**	**B**	**C**
DO (% saturation)	Mean	94.014	92.827	91.062	83.257
	SD	6.788	7.157	8.11	14.683
	10 percentile	84.56	83.66	80.67	64.44
	Grade	**A**	**A**	**A**	**C**
Ammonia (mg N / l)	Mean	0.118	0.177	0.229	0.396
	SD	0.140	0.133	0.250	0.549
	90 percentile	0.25	0.334	0.481	0.874
	Grade	**A**	**B**	**B**	**C**
Suspended sediment (mg / l)	Mean	10.651	12.173	9.374	6.974
	SD	13.834	8.897	9.107	7.090
	90 percentile	17.1	25.0	16.8	12.8
COD (mg / l)	Mean	18.877	24.560	27.814	31.429
	SD	22.743	23.850	32.116	27.383
	90 percentile	42.4	35.38	59.76	56.996

Table 1: Chemical GQA classification & biochemical parameters: Charlton Brook.

4.2. Metals

Stormwater metals analyses have demonstrated highly elevated concentrations compared to background water samples (Table 2). Aluminium, cadmium and chromium are particularly indicated, with mean values exceeding those reported in motorway runoff by others (Maltby et al, 1995). Average stormwater values at the catchment outlet (g), site exceeded the United States' EPA Criteria Maximum Concentration for aluminium, cadmium and copper. Background water levels for cadmium and lead also exceed the EPA's Criteria Continuous Concentration limits for aquatic life (U.S. EPA, 1986). Water quality criteria for individual chemicals represent levels, that when exceeded, may harm aquatic organisms. Because criterion values are only available for individual chemicals, alternative models are necessary to estimate toxic effects of metal mixtures (Clements *et* al., 2000), hence their derivation of the CCU. The EPA metal thresholds are based on toxicity tests of species from different trophic levels, including macroinvertebrates (Hirst et al., 2002).

Metal (µg / l)	EPA aquatic life criteria (hardness adjusted)* CCC	Charlton Brook Mean dry-weather flow concentration (site g)	EPA aquatic life criteria (hardness adjusted)* CMC	Charlton Brook Average Storm EMC (site g)
Aluminium	87	6.9	750	886.3
Cadmium	0.32	0.3	2.8	5.2
Chromium	97.63	---	750.5	19.9
Copper	11.94	3.1	18.5	26.8
Iron	1000	60.7	---	1759.5
Lead	3.6	21.1	93	25.6
Manganese	1000	65.9	---	292.6
Nickel	69	1.5	622	7.1
Silver	---	---	5.7	1.1
Zinc	157	3.5	156	47.0

Table 2: Concentrations of metals in discharges to Charlton Brook.

* Source: 'The Gold Book' (Quality Criteria for Water: 1986, EPA 440/5-86-001) and subsequent amendments; National Recommended Water Quality Criteria - Correction, 1999, EPA-822-Z-99-001 & National Recommended Water Quality Criteria: 2002, EPA-822-R-02-047.

At all sites, CCU scores greater than 1 were determined, a level at which, if exceeded, represents a conservative estimate of the total metal concentration likely to cause harm to aquatic organisms (Clements et al., 2000). Winter scores ranged from 1.1 to 3.6, increasing on a gradient from upstream to downstream. Interpretation of the background water quality samples indicates that cadmium, lead and copper, were the major cause of potential impairment and to a lesser extent, aluminium and manganese. Lead, copper and cadmium accounted for 91 % of the mean CCU, yet in contrast, accounted for only 6.7 % of the total metal instream. Conversely, in absolute terms, manganese, iron and aluminium accounted for 89 % of the total metal instream, yet only 11% of the contribution to overall CCU score.

Mean Summer CCU scores showed that lead and cadmium remained major sources of potential toxicity, accounting for 88 % of the CCU, yet only 11 % of the total metal instream. The scores were significantly higher for the urbanised sites, ranging from 11 to 17, although the upstream reference site remained virtually unchanged at 1.15, with lead levels an order of magnitude less than at the urbanised sites. As an example, the relative percentage contribution of each metal to CCU score and instream metal loading at site g is

shown in Figure 2. The CCU scores for the Winter and Summer are shown in table 3.

Not surprisingly, the upstream site (a) had the lowest sediment levels of cadmium, chromium, copper, lead and zinc. However, individual metal concentrations did not vary significantly between the different urbanised sites. In terms of PEL metal levels, only chromium at site d exceeded the stated threshold (284 mg / kg dry wt.).

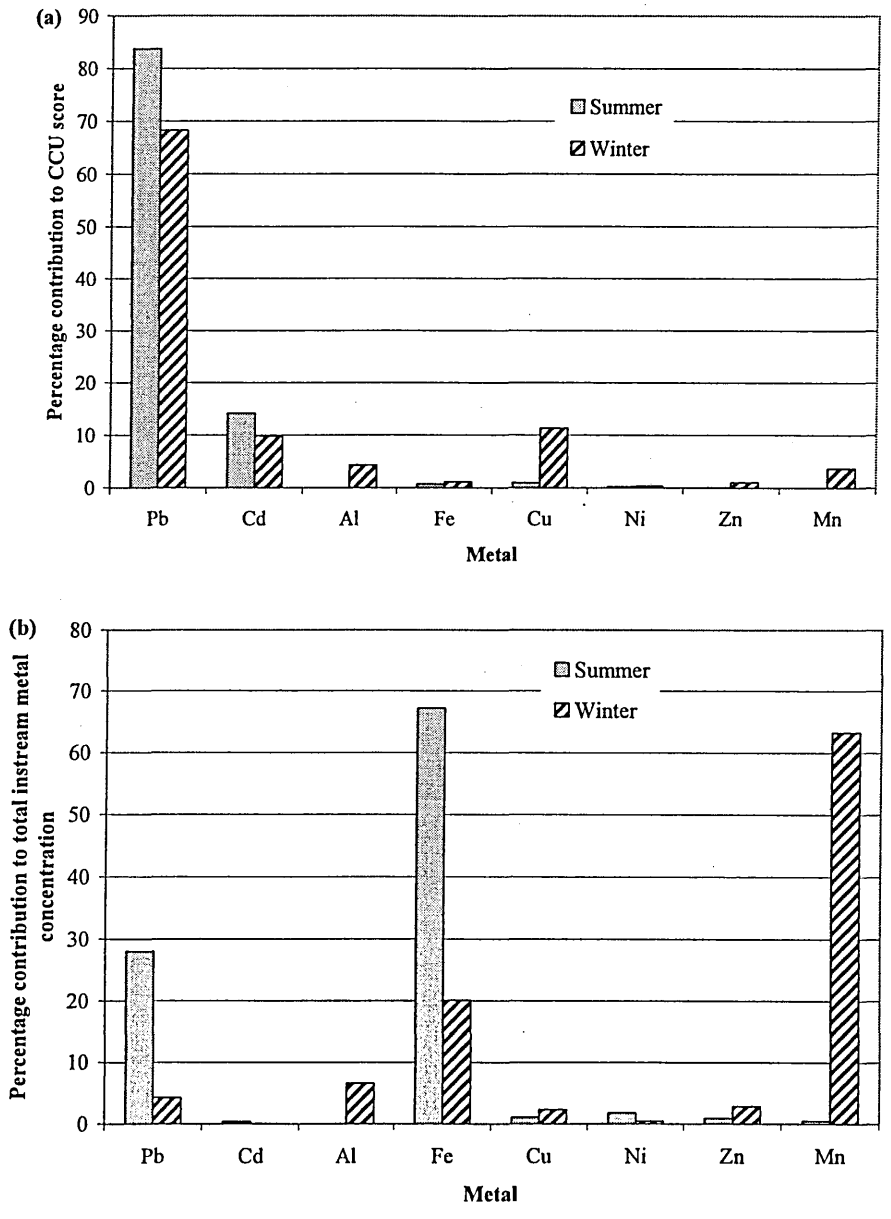


Fig 2: The relative contribution of individual metals to CCU score (a) and to total instream metal concentration (b) at site g, Charlton Brook.

CCU Scores	Site 1	Site 2	Site 3	Site 4	
Winter	1.11	2.49	2.52	3.61	
	Site a	Site d	Site e	Site f	Site g
Summer	1.15	17.04	11.86	11.3	11.03

Table 3: Winter & Summer CCU scores, Charlton Brook.

4..3. Organic micropollutants

Contaminated sediments contained between 2592 and 25,961 μg total hydrocarbons / kg dry wt. The dominant PAHs at the most contaminated site (*g*) were fluoranthene (5591 μg / kg dry wt.), pyrene (4726 μg / kg dry wt.) and phenanthrene (3812 μg / kg dry wt.), comparable to levels found in sediments contaminated by M1 motorway runoff (Maltby et al., 1995). Additionally, benz[a]anthracene and chrysene were elevated at the most downstream site (2483 μg / kg, and 2426 μg / kg respectively). Total PAHs peaked at sites *d* and *g* with concentrations of 13453 and 25961μg / kg dry wt. respectively. These two sites recorded 7 and 8 exceedencies for individual PAHs respectively. The ratios of different PAHs were used to infer the likely source of PAH contamination. For example, phenanthrene and anthracene are structural isomers, but anthracene originating from oil spills degrades more rapidly than from combustion. This is not the case for phenanthrene. Therefore, a low Phe / Ant ratio (<10) suggests that a greater proportion of the PAH contamination originates from pyrolitic sources (Wilson et. al., 2003). Fluoranthene and pyrene ratios can similarly be utilised with simultaneous study of the ratios allowing for the definition of two different classes of sediments: Phe / Ant (>10) and Flu / Pyr (>1) for petrogenic inputs and Phe / Ant (<10) and Flu / Pyr (<1) for the dominance of pyrolitic sources (Budzinsky et al., 1997 in Dahle et al., 2003). The phenanthrene / anthracene & fluorene / pyrene ratios occurring in the stream sediment samples are shown in (Figure 3), suggesting that combustion sources (vehicle engines) were more widespread and present within the catchment in greater quantities than oil spill sources.

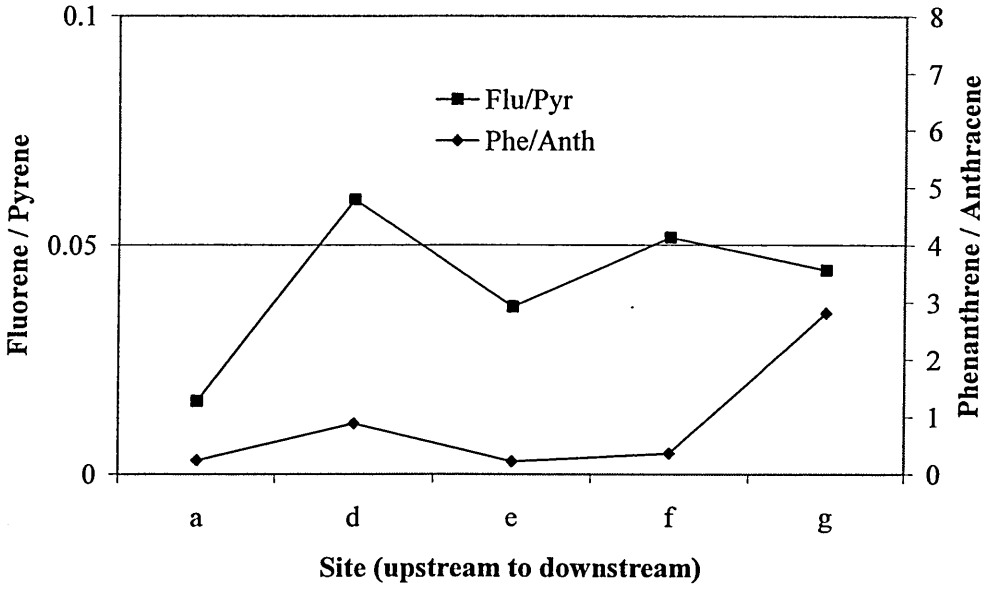


Fig. 3: PAH ratios indicating pyrolitic sources within the catchment.

PEL-quotient values varied throughout the watercourse (Figure 4), with all sites having the potential for adverse biological effects. The PEL approach has been shown to have a high reliability of predicting impairment with the probability of observing toxicity shown to be a function of both the number of substances exceeding the various guidelines as well as the degree to which they exceed the guidelines. (CSMWG, 2003). Significant differences between sites a, f and g in relation to sites d and g were confirmed in relation to normalised PEL quotient levels. The differences between sites d and g and between a, e & f were not significant. Table 4 shows the concentrations of pollutants for each of the sampled sites used in deriving the normalised PEL-quotients.

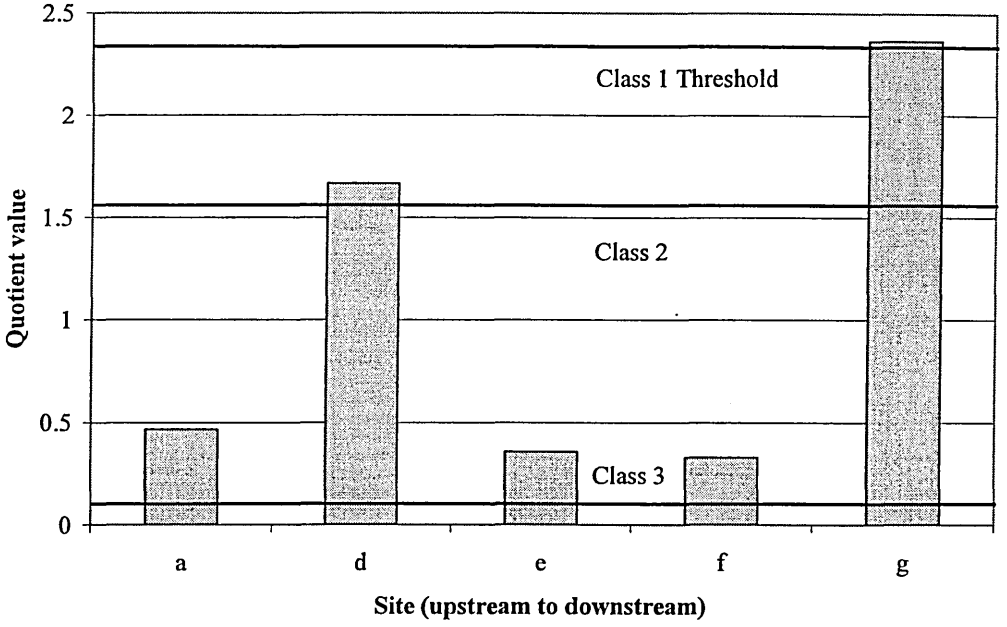


Fig. 4: Mean PEL-quotient values for Charlton Brook, with indicated threshold values.

Contaminant	Site a	Site d	Site e	Site f	Site g
Naphthalene (μg kg $^{-1}$)	51.90	8.85	79.57	29.26	43.05
Acenaphthylene (μg kg $^{-1}$)	3.08	29.33	9.42	3.45	26.04
Acenaphthene (μg kg $^{-1}$)	3.61	116.00	35.79	8.62	181.45
Fluorene (μg kg $^{-1}$)	8.58	134.49	27.63	14.43	210.76
Anthracene (μg kg $^{-1}$)	1023.21	2013.46	635.50	601.56	1353.58
Phenanthrene (μg kg $^{-1}$)	251.19	1784.68	144.17	219.49	3812.16
Fluoranthene (μg kg $^{-1}$)	516.32	2690.56	0.00	292.24	5591.95
Pyrene (μg kg $^{-1}$)	537.33	2242.14	754.67	278.78	4725.60
Benz[a]anthracene (μg kg $^{-1}$)	148.03	754.82	0.00	0.00	2482.83
Chrysene (μg kg $^{-1}$)	342.36	991.80	0.00	371.29	2425.61
Cadmium (mg kg $^{-1}$)	0.27	0.86	0.64	0.56	0.48
Chromium (mg kg $^{-1}$)	11.60	284.00	21.70	17.60	72.20
Copper (mg kg $^{-1}$)	3.90	22.40	6.30	15.00	17.70
Lead (mg kg $^{-1}$)	14.90	38.60	19.50	30.80	50.30
Zinc (mg kg $^{-1}$)	26.70	27.70	28.40	44.20	49.30
Normalised PEL-quotient	0.47	1.67	0.36	0.33	2.37

Table 4: Sediment concentrations of pollutants.

4.4. Macroinvertebrates

Biotic scores the upstream rural site were much higher than the urban sites, having a rich Ephemeroptera, Plecoptera, and Trichoptera assemblage.

Data for sites b & c was unobtainable for the Autumn sampling period. The ephemeral nature of the two streams meant that both had dried completely over the summer. Overall GQA grade, which incorporates environmental quality indices (EQIs; E.A., 2003) for the number of taxa and ASPT illustrate the decline in biological quality over the length of the watercourse (Table 5) with the additional diversity indices employed in the study confirming this trend.

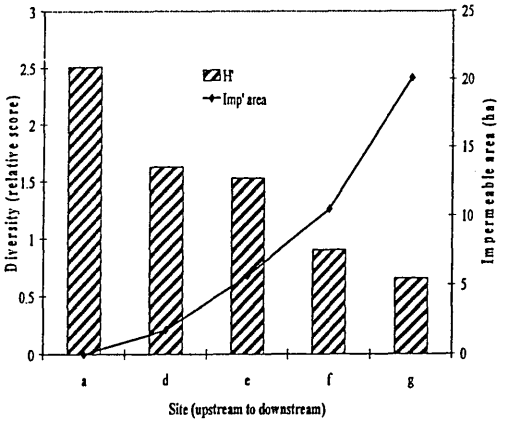
Site	**a**	**d**	**e**	**f**	**g**
BMWP	158	96	85	78	40
BMWP taxa	24	18	17	14	11
ASPT	6.58	5.33	5.0	5.6	3.64
O/E ASPT	1.34	1.09	1.02	1.15	0.74
O/E No. Taxa	0.99	0.76	0.71	0.59	0.46
GQA grade	**A**	**B**	**B**	**C**	**D**
Diversity (H')	2.51	1.63	1.53	0.90	0.66
Evenness (J')	0.76	0.65	0.58	0.34	0.26

Table 5: Biological GQA classification and diversity indice scores.

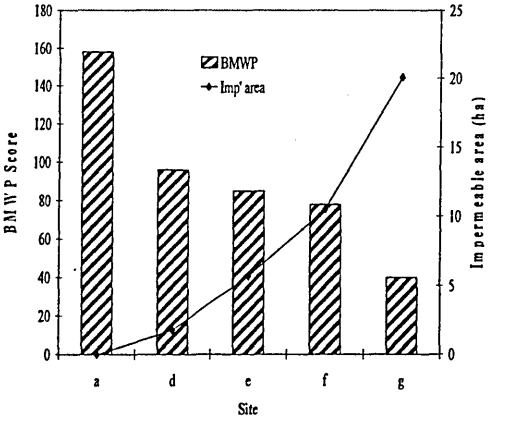
Sites *e, f* and *g* displayed clear signs of community instability with Assellidae (water hoglice) comprising 44, 62 and 46% of individuals present respectively. The percentage Ephemeroptera, Plecoptera and Tricoptera (EPT) declined from 41% of total assemblage at site *a* to 20% at site *g*, despite numbers being buoyed by the relatively tolerant mayfly Baetidae; the only family from the EPT group represented at all sites, and an indicator of declining water quality (Plotnikoff, 1998). Increased abundance of Baetidae within the mayfly assemblage is recognised as a response to stream impairment and in comparison to Heptagenidae, are more tolerant of metals, BOD and ammonia.

Figure 5. illustrates the percentage impermeable area of the catchment, which increases with each successive downstream outfall in relation to diversity and evenness indices. Compared with the biological data, this would appear to confirm that even small areal increases in impermeable area contribute to a measurable drop in biological quality, although the mechanisms behind this are not yet fully understood.

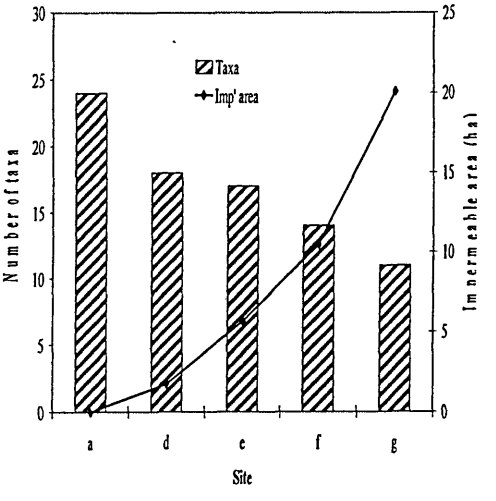
Comparison of impermeable area and diversity *H'*



Comparison of impermeable area and BMWP



Comparison of impermeable area and number of taxa



Comparison of impermeable area and evenness *J'*

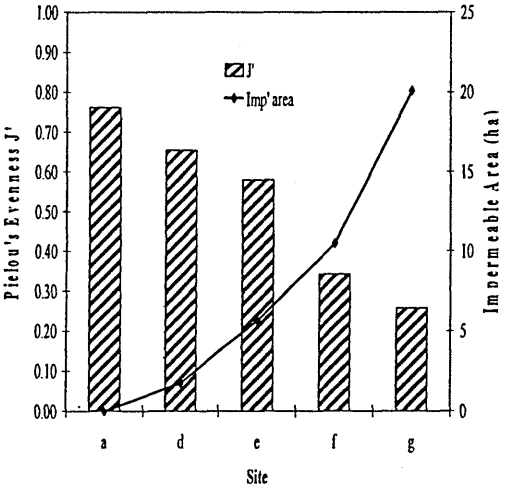


Fig. 5: Comparison of impermeable area with BMWP, evenness *J'*, number of taxa and diversity *H'*.

5. Discussion

The biotic ASPT and BMWP scores encapsulate the observed trend of a decreasing abundance of sensitive families with increasing abundance of pollution tolerant families such as Asellidae, suggesting the presence of

organic pollution, a well documented constituent of stormwater runoff (Hvitved-Jacobsen, 1986; House *et al.*, 1993). The increased abundance of Asellidae in the urban portion of the catchment was accompanied by an equivalent decline in Gammaridae (freshwater shrimps), possibly reflecting the greater sensitivity of gammarids to ammonia and other effluents (Mullis et al., 1996). However, this overall trend of reduced species richness, and a shift from sensitive to tolerant taxa may also be an indication of metal pollution (Clements, 1994), with the decline in number of taxa seen as a general indicator of overall pollution which includes organic and toxic pollution (E.A., 2003). Calculated diversity indices, which were typical of a stressed environment within the urbanised part of the catchment, support this. Evidence suggests that there is increasing tolerance to heavy metal pollution in the sequence from mayflies, to caddisflies to midges (Savage & Rabe, 1973; Winner et al., 1980) and the assemblage within Charlton Brook has mirrored this trend, lending support to the possibility that this is an ecological response to heavy metals within the watercourse. EPT abundance was strongly inversely related to copper and lead ($p = 0.037$, $p = 0.019$ respectively). However, there was no replacement of sensitive mayfly taxa by metal-tolerant species of caddis such as hydropsychidae, as has been reported elsewhere (Clements & Kiffney, 1994). Instream concentrations of cadmium and lead showed a significant negative correlation with all the stonefly families, Heptagenid mayflies and the Polycentropidae, Rhyacophilidae and Leptoceridae caddis families. Diptera larva are particularly sensitive to trace metals (Shutes, 1984) and although much reduced in comparison to the rural sites during the Spring, Tipulidae and Simulidae were absent from all urbanised sites during the Autumn sampling, possibly reflecting the increase in instream metal concentration. The chironomidae family however are reported as being unaffected by metals (Mason, 2002) and were present at all sites.

PAHs in conjunction with metals as a function of the PEL-quotient method employed, suggest that all the sites sampled for macroinvertebrates have the potential for being adversely affected by the pollutants contained within the brook's sediment. Mean PEL-quotients suggest that sediment contamination within the brook is indicated at all sites, with sites a, e & f, typified by 'localised areas of low to moderate contamination', site d with

'moderate to high contamination' and site g, 'widespread and high levels of contamination...with measured or observed impacts on species composition / diversity' (CSMWG, 2003). Although PEL-quotients displayed a significant negative correlation with EPT index (p = 0.028), the longitudinal decline in macroinvertebrate diversity was not matched by a commensurate increase in the putative toxic potential determined by use of the PEL system. Statistical analysis of mean PEL-quotient values and the impermeable areas associated with those surface water outfalls immediately upstream of sampling sites showed a significant correlation (p = 0.042), suggesting that sediment bound pollutants are in proportion to the impermeable areas from which they are generated whilst remaining fairly localised within the stream bed. Similarly, CCU scores whilst illustrating significant temporal differences between seasons, suggest potential chronic toxicity at all sites, particularly within the urbanised portion of the catchment. Although dissolved metal concentrations as utilised in the study are a better indicator of metal bioavailability than total recoverable metal, the criteria may still be somewhat overcautious. Metal toxicity to aquatic biota is dependant on a variety of ambient quality characteristics including hardness, pH, temperature, particulate and dissolved organic matter. For example, an increase in toxicity would be expected with a decrease in pH so, as pointed out elsewhere (Hirst *et al.* 2002), refinements to the CCU scores to account for the effects on metal toxicity at varying pH would seem desirable.

Stormwater discharges to watercourses can have numerous impacts, although their intermittent and unpredictable nature means that regular chemical sampling, typically practiced during low flows, often fails to detect high chemical and suspended sediment inputs. Hydrometric data reveals that the catchment experienced 430 separate rainfall events between March 2002 and January 2004; the period encompassing the GQA-based sampling; however, all samples were obtained during dry-weather flow conditions. During sampled storm events (Figure 6), the watercourse, taken as a point-source discharge to the next river, produced pollutant concentrations in exceedance of EC standards for sewage discharges following secondary treatment. In the absence of acute water quality criteria, storm pollutant

concentrations were compared to the U.S. EPA Criteria Maximum Concentration standards (EPA, 1986). All measured storms exceeded the 1-hour maximum concentration set by the EPA for copper, the major aquatic toxic metal in stormwater (Dannecker et al., 1990), with cadmium exceeding the standard in 80 % of cases and aluminium in 60 % of cases.

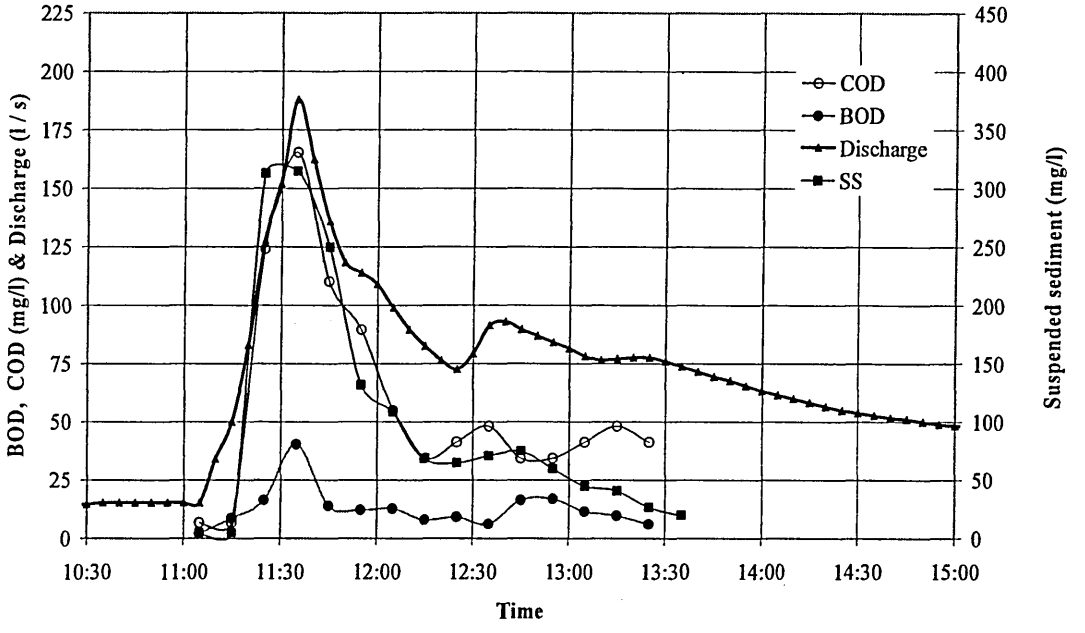


Fig. 6: Measured biochemical parameters for storm event of 21st July.

Hydraulic modelling of the stormwater drainage network within the catchment using Hydroworks™ (Figure 7), has demonstrated that water at the start of the storms is associated with the SWOs and that the elevated pollutant loadings are similarly associated with the start of the storms (Figures 6 & 8). Low baseflows effectively mean that there is no dilution of pollutants associated with SWOs within the brook. Modelling of the drainage network has also demonstrated increasing instream discharge with each successive outfall. Whilst this does not necessarily translate into increasing pollutant concentration along the length of the watercourse, the duration of exposure to instream pollutants does. Results indicate that the mismatch between chemical and biological grade as a likely consequence of SWO discharges is similar to that found as a result of polluted surface water outfalls and CSOs

(Faulkner et. al, 2000). As even a small load may produce an unacceptable concentration in a small stream where the capacity for dilution is limited (House et al., 1993), the concept of dilution volumes in receiving waters may not be applicable to unclassified watercourses; rather this is a feature of the receiving river downstream.

Prima facie evidence suggests that both CCUs and mean PEL - quotients may be beneficial in determining whether the potential for toxicity exists. The biological indices support this view. However, with the exception of stoneflies, there was a significant lack of correlation between macroinvertebrates and individual pollutants and / or the cumulative measures of toxicity employed. Significantly, diversity was inversely correlated with increasing impermeable area although the reasons for this in relation to multiple stormwater inputs demand further investigation.

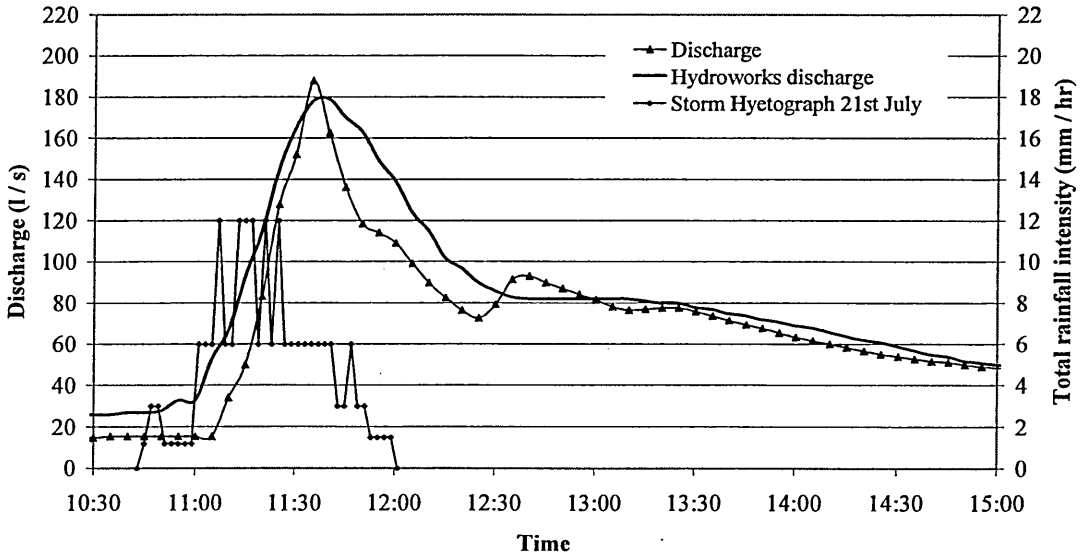


Fig. 7: Storm hyetograph of 21st July 2003 with comparison of measured discharge and Hydroworks simulation.

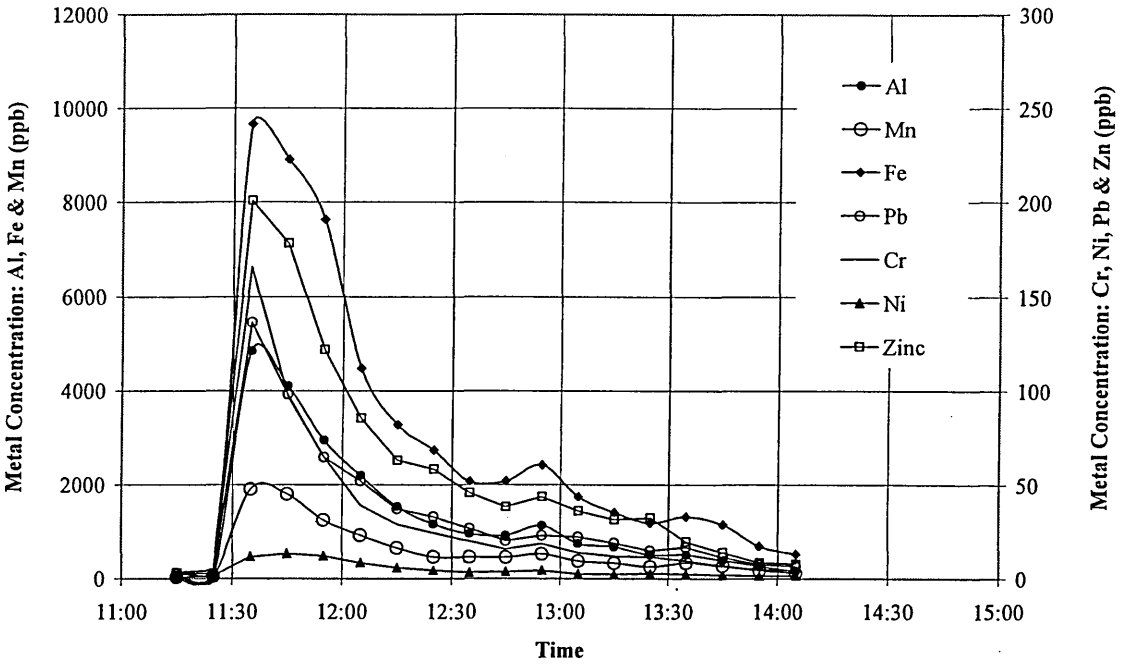


Fig. 8: Graph of selected metals from the storm of 21st July 2003.

6. Conclusions

Benthic macroinvertebrate analysis has demonstrated a greater deterioration over the length of the watercourse than that suggested by the GQA chemical analysis alone and a marked decline in biological integrity with the onset of urbanisation.

Other than SWOs there are no other discharges to the brook, which experiences frequent storm induced discharges of a quality that likely exceed limits set for secondary treated sewage effluent.

Overall, the effect is of declining biological quality with successive increases in impermeable area. Data indicate that the exposure of invertebrates to storm discharges will increase in duration with each successive outfall.

Further work is required on Charlton Brook in order to understand the range of frequency, duration and pollutant concentration of storm discharges in relation to precipitation and catchment characteristics.

Acknowledgements

The work described in this paper was carried out under a research studentship funded by the School of Environment and Development, Sheffield Hallam University. Additional technical assistance has been given by Messrs. P. Flanagan, P. Collins, L. Goodwin, T. Robson and Mrs J. Hague, of Sheffield Hallam University.

References

Baker DM. Yousef YA. Metal Accumulation and Impacts on benthic organisms in Detention Pond Sediments. Fourth Biennial Stormwater Research Conference. Clearwater, Florida, 1995.

Beasley G, Kneale P. Reviewing the impact of metals and PAHs on macroinvertebrates in urban watercourses, Progress in Physical Geography, 2002; 26[2]: 236 - 270.

British Standards Institute. BS 3680-4A: Measurement of liquid flow in open channels - Part 4A: Method using thin-plate weirs. London, British Standards Publications Limited, 1981.

Burton GA. Pitt RE. Stormwater Effects Handbook: A Toolbox for Watershed Managers, Scientists, and Engineers. Lewis Publishers, London, 2002, 911 pp.

CCME. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. Environment Canada, Guidelines Division, Ottawa, CCME EPC-98E, 1998.

Clements WH. Benthic Invertebrate Community Responses to Heavy Metals in the Upper Arkansas River Basin, Colorado, Journal of the North American Benthological Society 1994; 13[1]: 30-44.

Clements WH, Carlisle DM, Lazorchak JM, Johnson PC. Heavy metals structure benthic communities in Colorado mountain streams, Ecological Applications 2000; 10: 626-638.
Clements WH. Kiffney PM. Integrated laboratory and field approaches for assessing impacts of heavy metals at the Arkansas River, Colorado, Environmental Toxicology and Chemistry 1994; 13: 397-404.

CSMWG. A Method for Ranking Contaminated Aquatic Sites on Canadian Federal Properties 2003. Government of Canada, Ottawa.

Dahle S, Savinov VM, Maishov GG, Evenset A, Næs K. Polycyclic aromatic hydrocarbons (PAHs) in bottom sediments of the Kara Sea shelf, Gulf of Ob and Yenisei Bay, The Science of the Total Environment 2003; 306: 57-71.

Dannecker W, Au M, Stechmann H. 1990, Substance load in rainwater runoff from different streets in Hamburg, The Science of the Total Environment 1990; 93: 385.

DETR. First Consultation Paper on the Implementation of the EC Water Framework Directive, Department of the Environment Transport and Regions, London 2001.

DETR & Buildings Regulations Division. The Building Act 1984: Review of Part H (Drainage and Solid Waste) of the Building Regulations 1991 and associated legislation. HMSO, London, 2000.

Ellis JB, Hvitved-Jacobsen T. Urban Drainage Impacts on Receiving waters. Journal of Hydraulic Research 1996; 34[6]: 771-783.

Enserink EL, Maas-Diepeveen JL, Van Leeuwen CJ. Combined effects of metals; an ecotoxicological evaluation. Water Research 1991; 25[6]: 679-687.

Environment Agency. The State of the Environment of England and Wales: Fresh Waters HMSO, London, 1998.

Environment Agency. General Quality Assessment of Rivers: Biology, Bristol, 2003.

Faulkner H, Edmonds-Brown V, Green A. Problems of Quality designation in Diffusely Polluted Urban Streams - The Case of Pymme's Brook. Environmental Pollution 2000; 109: 91-107.

Furse MT. The application of RIVPACS procedures in headwater streams - an extensive and important national resource. In: Wright JF, Sutcliffe, Furse MT, editors. Assessing the biological quality of fresh waters: RIVPACS and other techniques, Freshwater Biological Association, Ambleside 1997, pp 79-91.

Gower AM, Myers G, Kent M. Foulkes ME. The use of macroinvertebrate assemblages in the assessment of metal-contaminated streams. In D. M. Harper & A. J. D. Ferguson, editors. The Ecological Basis for River Management, Wiley, Chichester, 1995, pp 181-191.

Hall MJ, Hockin DL, Ellis JB. *Design of Flood Storage reservoirs*, CIRIA & Butterworth-Heinemann Ltd, Oxford, 1993, 187 pp.
Hirst H, Juttner I, Ormerod SJ. Comparing the responses of diatoms and macroinvertebrates to metals in upland streams of Wales and Cornwall. Freshwater Biology 2002; 47: 1752-1765.

House MA, Ellis JB, Herricks EE, Hvitveld-Jacobsen T, Seager J, Lijklema L, Aalderink RH, Clifforde I. Urban Drainage - Impacts on Receiving Water Quality. Water Science and Technology 1993; 27[12]: 117-158.

Hvitved-Jacobsen T. Conventional Pollutant Impacts on Receiving Waters. In Torno HC, Marsalek J, Desbordes M, editors. Urban Runoff Pollution, 1st edn, Springer-Verlag, Berlin, 1986.

Hvitved-Jacobsen T, Yousef YA. Highway runoff quality, environmental impacts and control. In: Hamilton RS, Harrison RM editors. Highway Pollution, Elsevier, London, 1991.

Lau J, Butler D, Shutze M. Is combined sewer overflow spill frequency / volume a good indicator of receiving water quality impact? Urban Water 2002; 4[2]: 181-189.

Long ER, MacDonald DD. Effects Range Low and Median, Threshold and Probable Effects Levels, in Use of Sediment Quality Guidelines in the Assessment and Management of Contaminated Sediments, SETAC Press, 1997.

Ludwig JA, Reynolds JF. Statistical Ecology: A Primer on Methods and Computing John Wiley & Sons, Chichester, 1988, 337 pp.

Makepeace DK, Smith DW, Stanley SJ. Urban Stormwater Quality: Summary of Contaminant Data, Environmental Science and Technology 1995; 25[2]: 93-139.

Maltby L, Forrow DM, Boxall ABA, Calow P, Betton CI. The Effects of Motorway Runoff on Freshwater Ecosystems: Field Study, Environmental Toxicology and Chemistry 1995; 14: 1079-1092.

Mason CF. Biology of Freshwater Pollution, Pearson Education, Harlow, 2002.

MINITAB. MINITAB reference Manual, Release 8 edn, Minitab Inc, 1991.

Mullis RM, Revitt DM, Shutes RBE. A Statistical approach for the Assessment of the Toxic Influences on Gammarus Pulex (Amphipoda) and Asellus Aquaticus (Isopoda) Exposed to Urban Aquatic Discharges, Water Research 1996; 30[5]: 1237 - 1243.

Novotny V. Nonpoint Pollution and Urban Stormwater Management Technomic Publishing Co. Inc, Lancaster, 1995.

Payne JA. Assessment of the Impact of Discharges From Surface Water Sewers on Receiving Water Quality, PhD, Aston University, 1989.

Perdikaki K, Mason CF. Impact of Road Runoff on Receiving Streams in Eastern England, Water Research 1999: 33[7]: 1627-1633.

Saget A, Gromaire-Mertz MC, Deutsch JC, Chebbo G. Extent of Pollution in Urban Wet Weather Discharges, Wiley & Sons, 1998.

Savage NL, Rabe FW. The effects of mine and domestic wastes on macroinvertebrate community structure in the Coeur d'Alene River, Northwest Science 1973; 47: 159-168.

Standing Committee of Analysts. Suspended, settleable and total dissolved solids in waters and effluents. Methods for the examination of waters and associated materials., HMSO, London, 1980.

Standing Committee of Analysts. Ammonia in Waters: Methods for the examination of waters and associated materials, HMSO, London, 1981.

Standing Committee of Analysts. Chemical Oxygen Demand (dichromate value) of polluted and waste waters: Methods for the examination of waters and associated wastewaters, HMSO, London, 1986.

Standing Committee of Analysts. 5 Day Biochemical Oxygen Demand (BOD5): Methods for the Examination of Waters and Associated Materials, HMSO, London, 1988.

Seager J, Abrahams RG. The Impact of Storm Sewage Discharges on the Ecology of a Small Urban River, Water Science and Technology 1990; 22[10-11]: 163-171.

Shutes RBE. The Influence of Surface Runoff on the Macro-invertebrate Fauna of an Urban Stream, The Science of the Total Environment 1984; 33: 271-282.

Sriyaraj K, Shutes RBE. An assessment of the impact of motorway runoff on a pond, wetland and stream, Environment International 2001: 26: 433-439.

Transport Research Laboratory, DWW (Netherlands), VTI (Sweden), VTT (Finland), DRI (Denmark), LCPC (France), & LNEC (Portugal). Pollution from Roads and Vehicles and Dispersal to the Local Environment: Final report and Handbook, European Commission, POLMIT RO-97-SC.1027, 2002.

U.S. EPA. Quality Criteria for Water, Office of Water, U.S. Environmental Protection Agency, Washington, DC, USA, EPA 440/5-86-001, 1986.

U.S. EPA. National Water Quality Inventory 1988 Report to Congress Washington, DC, EPA/440/4-90/003, 1990.

U.S. EPA. Method 3540C: Soxhlet Extraction. Environmental Protection Agency: Office of Water, 1996.

U.S. EPA. National Recommended Water Quality Criteria - Correction, EPA-822-Z-99-001, 1999.

U.S. EPA. National Recommended Water Quality Criteria: 2002, EPA-822-R-02-047, 2002.

U.S. EPA. Method 610 - Polynuclear Aromatic Hydrocarbons. Environmental Protection Agency: Office of Water, 2003.
Wagner A, Geiger WF. 1996, New Criteria for Stormwater Discharges Into Urban Streams, Water Science and Technology, 1996; 34[3-4]: 41-48.

Wilson C, Clarke R. Persistent Pollutants in freshwater Sediments. Report for SEPA Diffuse Pollution Initiative. DPI Report No. 7, 2003.

Winner RW, Boesel MW, Farrell MP. Insect Community Structure as an Index of Heavy Metal Pollution in Lotic Ecosystems, Canadian Journal of Fisheries and Aquatic Science, 1980; 37: 647-655.