Stream quality in a small urbanised catchment

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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 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 from regular low flow sampling indicate a significant drop in quality downstream of the SWOs that discharge to the study watercourse. The decline in biological quality however, is greater than that suggested by physico-chemical analysis alone.

A marked drop in biological diversity was noted with the onset of urbanisation. Ecological Quality Indices (EQIs) derived from the River Invertebrate Prediction and Classification System (RIVPACS) predictions in conjunction with diversity and evenness indices show a deterioration in quality between the upstream rural and downstream urban portions of the catchment. There was a significant 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, a newly defined rating of total instream metal concentration as a function of suggested toxic thresholds. 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 significantly 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.

Keywords: Macroinvertebrates; Stormwater; Unclassified rivers; CCU; Water quality.

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1. Introduction

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). 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, possibly continuing to be the preferred option, resulting in a further deterioration of in-stream quality over this period, 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 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.

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 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 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 newly defined measure of total metal concentration and toxicity. It is calculated for any site as the ratio of the stream metal concentration to the U.S. Environmental Protection Agency criterion continuous concentration (CCC) values for toxicity (USEPA, 1986), the ratios being summed for all metals measured. 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:

$$\mathrm{CCU} = \sum m_i / c_i$$

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 has 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 PEL-quotient is derived thus:

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

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 Fig. 1). There was evidence of a small quantity of sewer litter downstream of outfall 15, 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% of the catchment with a total impermeable area of 20.09 hectares. The impermeability of this 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 (Fig. 2). 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 (figs. 1 and 2). Water samples (2-L) were taken for chemical analysis on a fortnightly basis between January 2002 and September 2003 to give a sufficient number of samples during the study period. Interrogation of the flow monitoring equipment confirmed that the watercourse was experiencing low-flows 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. 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).

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, Fig. 2) 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 (Fig. 2) using a rectangular thin-plate weir, installed to BS 3680-4A: 1981, 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 (fig. 1). The rain gauge at site RG1 was accompanied by a 'Snowdon' daily raingauge for calibration purposes.

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 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.

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).

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 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.

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. Unexpectedly, 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. The relative percentage contribution of each metal to CCU score and instream metal loading is shown in Figure 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.).

4.3. Organic micropollutants

Contaminated sediments contained between 2592 and 25,961 μg total hydrocarbons / kg wet wt. 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., 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 (Fig. 4), suggesting that combustion sources (vehicle engines) were more widespread and present within the catchment in greater quantities than oil spill sources.

PEL-quotient values varied throughout the watercourse (Fig 5), 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.

4.4. Macroinvertebrates

Biotic scores the upstream rural site were much higher than the urban sites, having a rich Ephemeroptera (mayfly), Plecoptera (stonefly), and Trichoptera (caddisfly) 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 3) with the additional diversity indices employed in the study confirming this trend.

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. 6 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. A significant negative correlation existed between increasing impermeable area and the Shannon-Weiner diversity index (p = 0.028,). A significant correlation was also found between impermeable area and number of taxa (p = 0.012). A negative though non-significant correlation was found in respect of ASPT (p = 0.055), suggesting that measures which incorporate the potential for harm from all pollutants are a better indicator of impacts within urban settings.

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 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 (-0.918, $p = 0.028$), 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 (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. 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.

The deterioration of biochemical quality at low flow may be explained by the frequent stormwater inputs of organic matter, sediments and organic micropollutants exerting a delayed oxygen demand. The impact from these inputs may persist for several days (Hvitved-Jacobsen, 1986) with subsequent storm events occurring before the stream has had time to fully recover. Chronic pollutant exposures from inorganic contaminants were likewise indicated from the study data.

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, 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. Figure. 7 illustrates this in relation to the storm of 21st July 2003). 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.

Hydraulic modelling of the stormwater drainage network within the catchment using Hydroworks™ (Fig. 8), 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 (Fig. 9). 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, there was a significant lack of correlation between macroinvertebrates and individual pollutants and / or the cumulative measures of toxicity employed.

Significantly, diversity correlated with increasing impermeable area although the reasons for this in relation to multiple stormwater inputs demand further investigation.

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.

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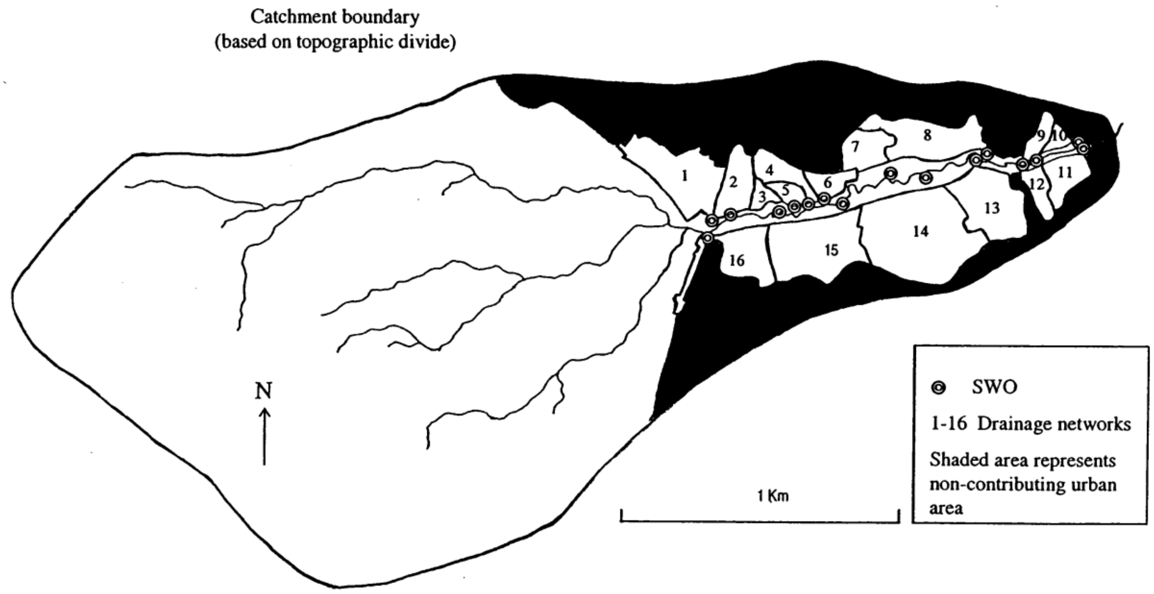

Fig. 1: Surface water outfall and drainage network location, Charlton Brook.

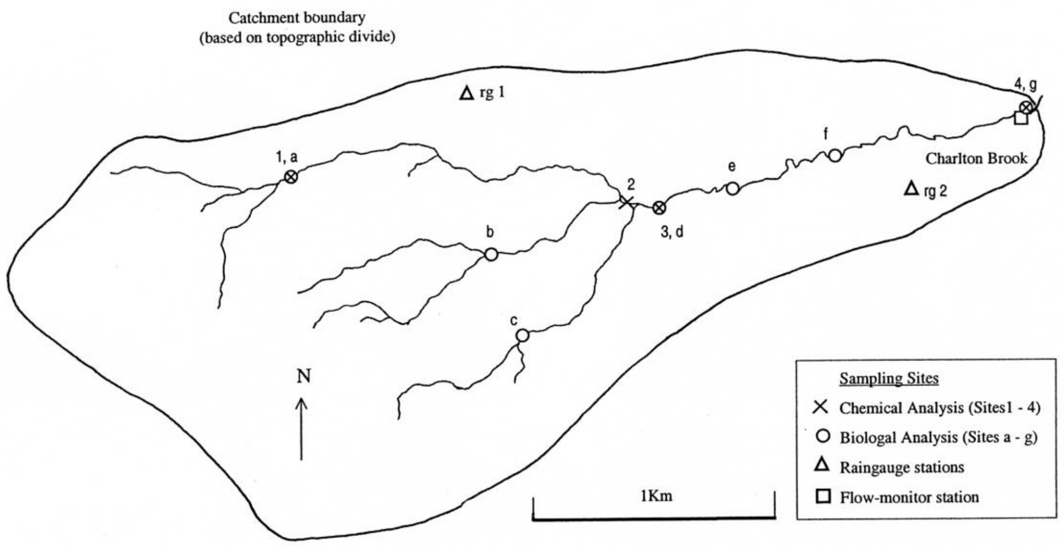

Fig. 2: Biological and physico-chemical sampling points, Charlton brook.

Parameter	Result	Site 1	Site 2	Site 3
BOD (mg / l)	Mean	1.315	1.596	2.250
	SD	0.647	0.662	0.862
	90 percentile	2.24	2.18	3.34
	Grade	**A**	**A**	**B**
DO (% saturation)	Mean	94.014	92.827	91.062
	SD	6.788	7.157	8.11
	10 percentile	84.56	84.96	82.72
	Grade	**A**	**A**	**A**
Ammonia (mg N / l)	Mean	0.118	0.177	0.229
	SD	0.140	0.133	0.250
	90 percentile	0.25	0.33	0.48
	Grade	**A**	**B**	**B**
Suspended sediment (mg / l)	Mean	10.651	12.173	9.374
	SD	13.834	8.897	9.107
	90 percentile	17.1	25.0	16.8
COD (mg / l)	Mean	18.877	24.560	27.814
	SD	22.743	23.850	32.116
	90 percentile	42.4	35.38	59.76

Table 1. Final GQA classification & biochemical parameters: Charlton Brook.

Metal (µg / l)	EPA aquatic life criteria (hardness adjusted)* CCC	Charlton Brook Mean dry-weather flow concentration	EPA aquatic life criteria (hardness adjusted)* CMC	Charlton Brook Storm EMC
Aluminium	87	7.2	750	886.3
Cadmium	0.32	0.3	2.8	5.2
Chromium (3)	97.63	5.1	750.54	19.9
Copper	11.94	3.6	18.5	26.8
Iron	1000	178.3	---	1759.5
Lead	3.6	17.2	93	25.6
Manganese	1000	58.8	---	292.6
Nickel	69	1.3	622	7.1
Silver	---	0.243	5.7	
Zinc	157	2.86	156	47.0

* 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.

Table 2. Concentrations of metals in discharges to Charlton Brook.

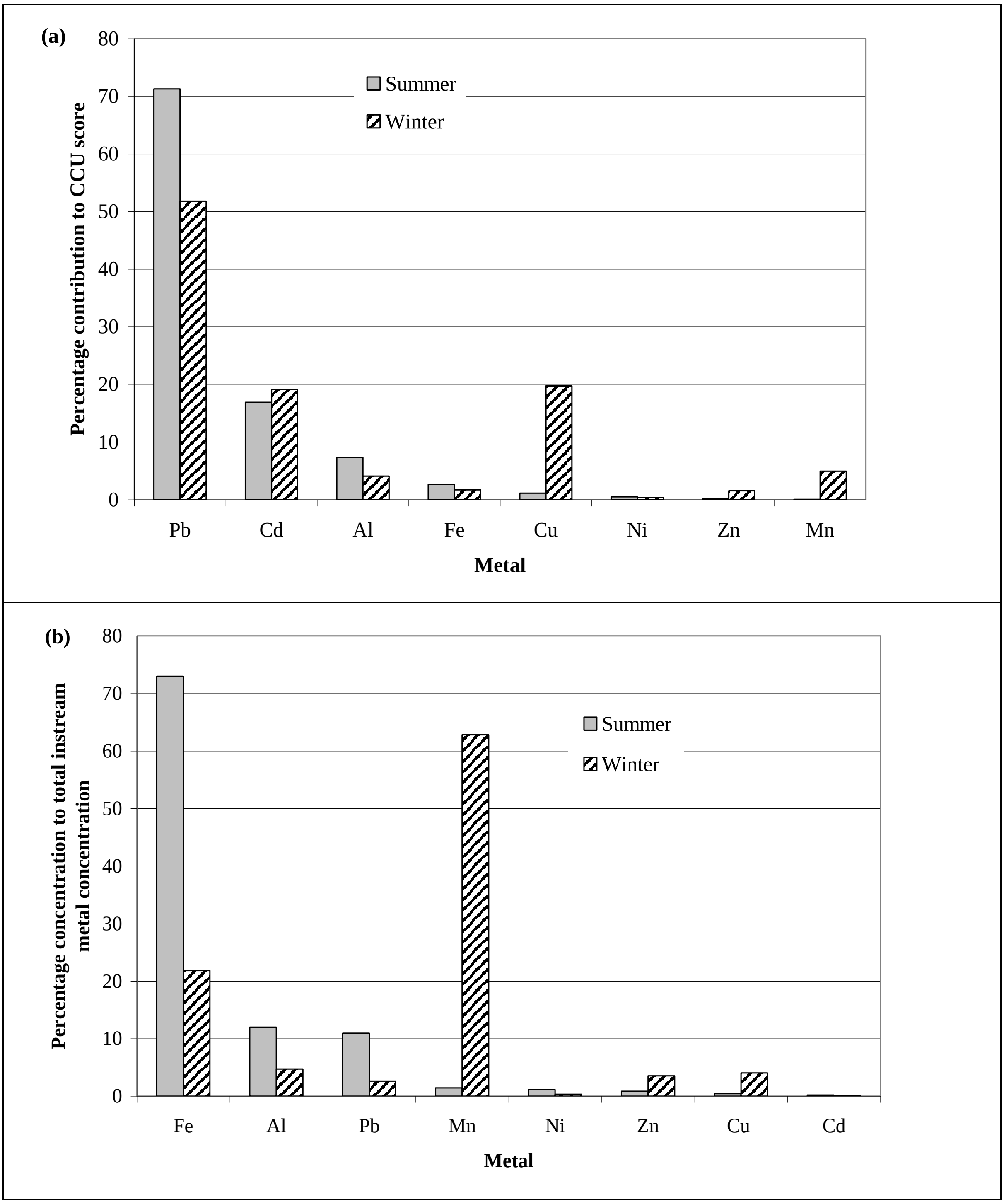

Fig. 3 The relative contribution of individual metals to CCU score (a) and to total instream metal concentration (b).

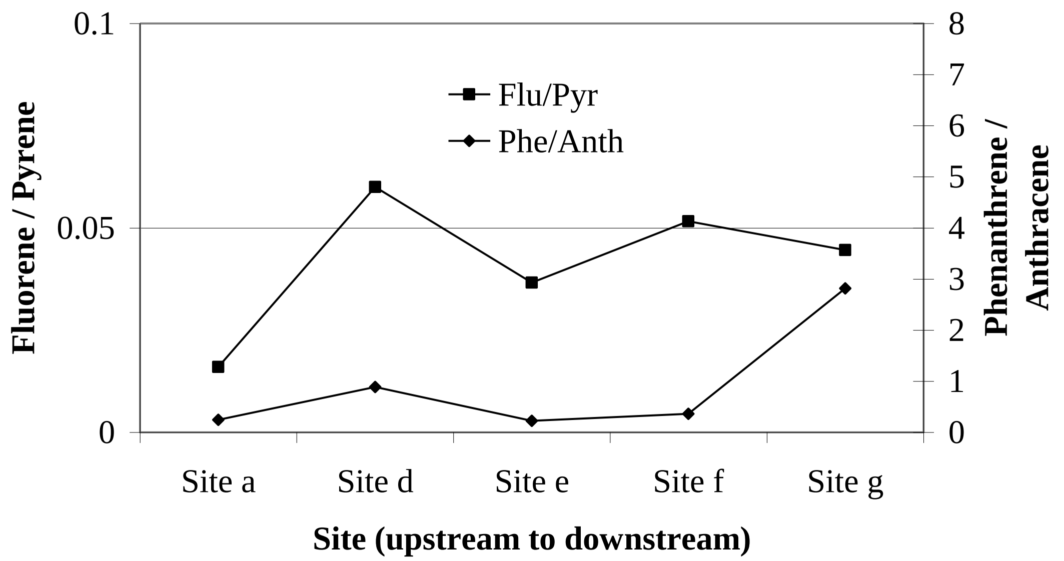

Fig. 4: PAH ratios indicating pyrolitic sources within the catchment.

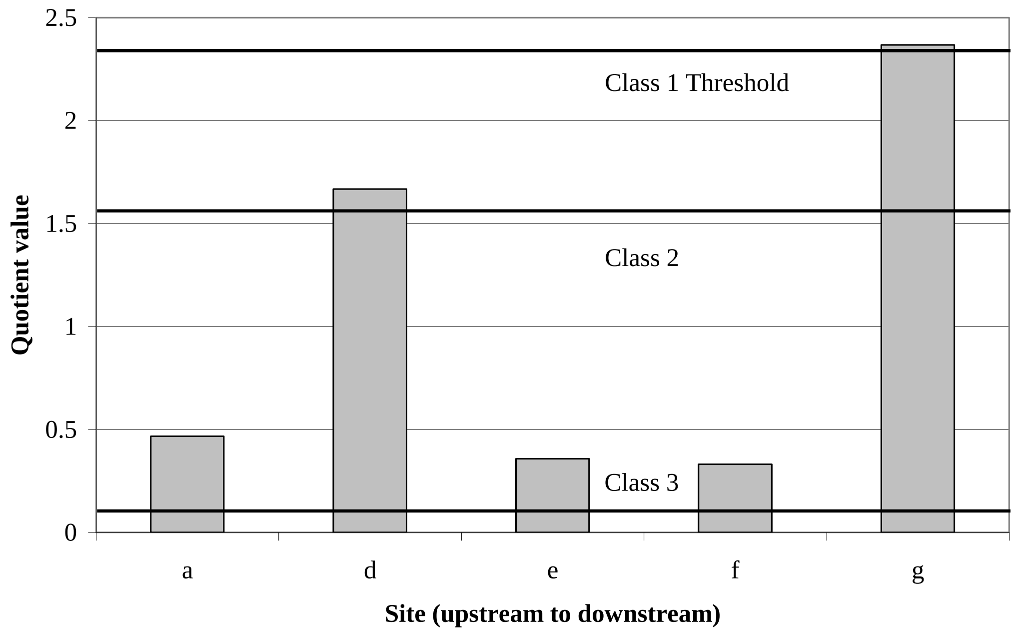

Fig. 5: Mean PEL-quotient values for Charlton Brook, with indicated threshold values.

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**
No' of families	29	21	20	15	14
Diversity (H')	2.63	2.08	1.83	1.38	1.53
Evenness (J')	0.73	0.59	0.52	0.53	0.41

Table 3: GQA derived grades and diversity indice scores.

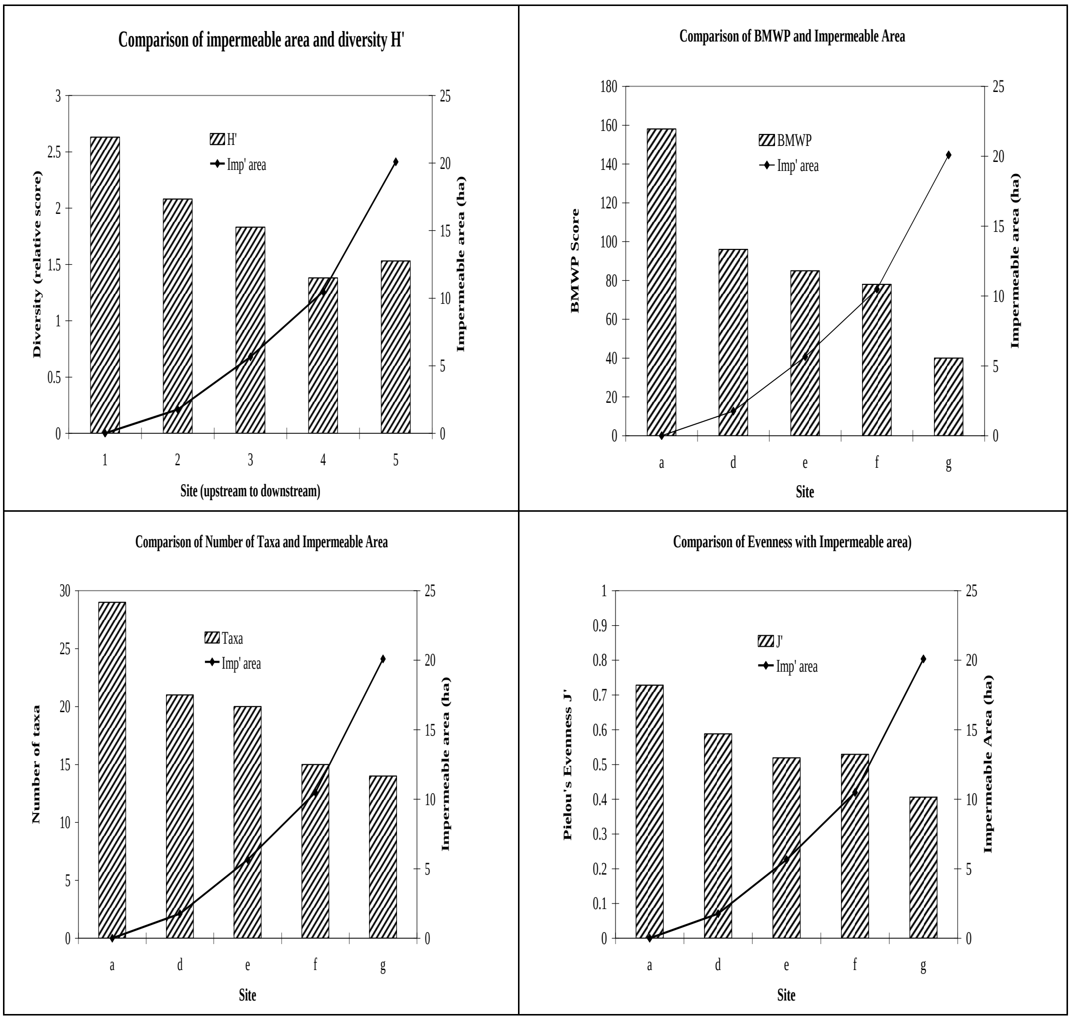

Fig. 6: Comparison of impermeable area with BMWP, evenness *J'*, number of taxa and diversity *H'*.

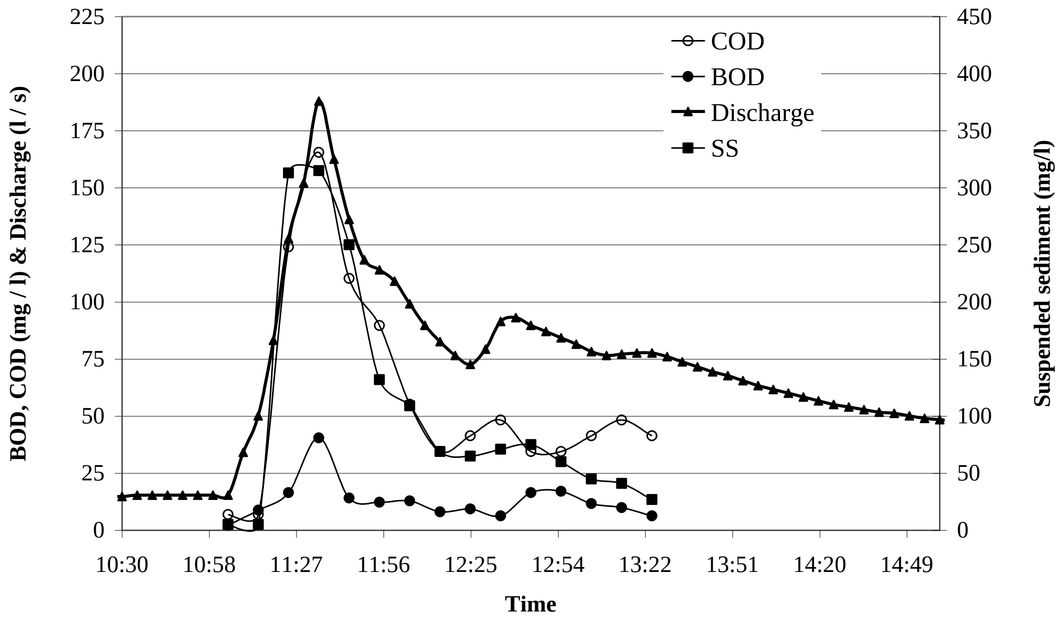

Fig. 7: Measured biochemical parameters for storm event of 21st July.

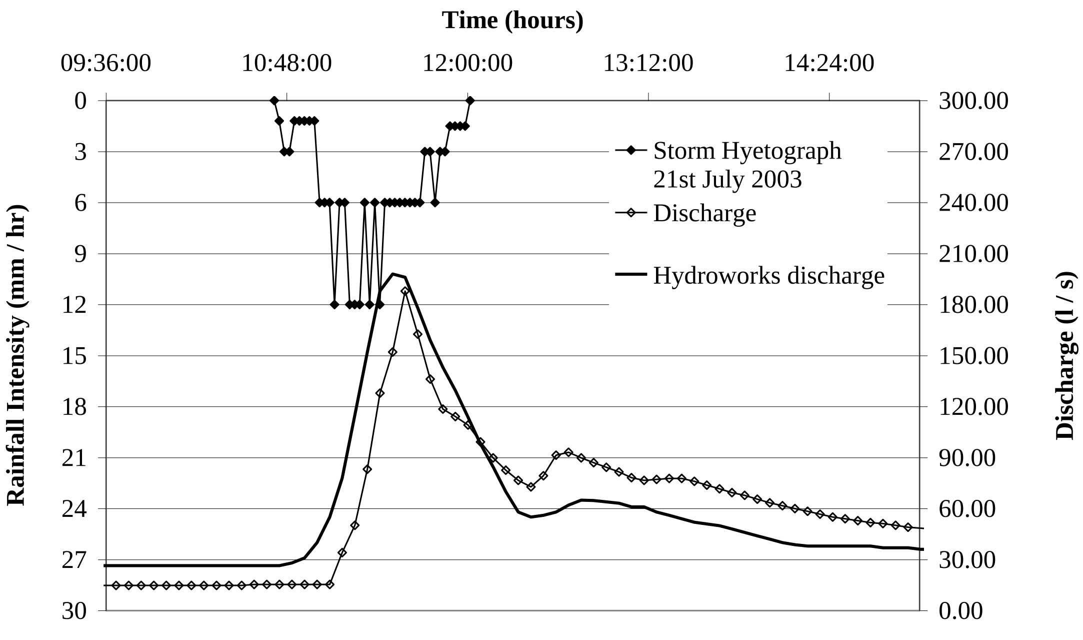

Fig. 8: Storm hyetograph of 21st July 2003 with comparison of measured discharge and Hydroworks simulation.

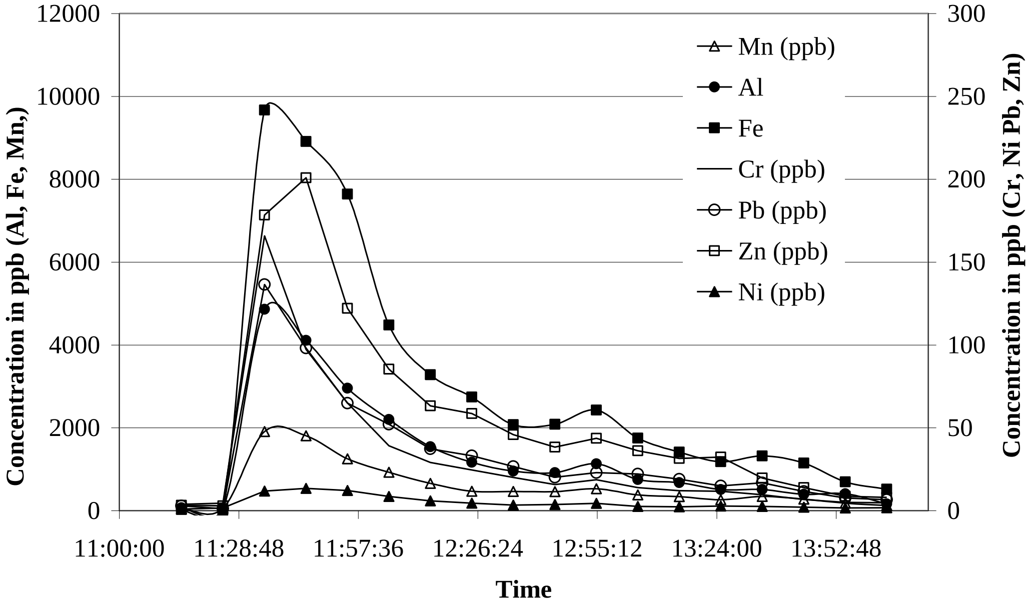

Fig. 9: Graph of selected metals from the storm of 21st July 2003.

List of potential referees

Captions to figures

Figure 1. Biological and physico-chemical sampling points, Charlton Brook.

Figure 2. Surface water outfall and drainage network location, Charlton Brook.

Figure 3. Storm hyetograph of 18th March 2002.

Figure 4: Plot of storm discharge, velocity and depth.

Figure 5: Storm data of 18th March 2002.

Figure 6: Comparison of impermeable area, BMWP and ASPT.

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