**Monograph:**
Beasley, G. and Kneale, P. (2001) Macroinvertebrates, Heavy Metals and PAHs in Urban Watercourses. Working Paper. School of Geography , University of Leeds.

School of Geography Working Paper 01/07

**WORKING PAPER**

**01/07**

# Macroinvertebrates, Heavy Metals and PAHs in Urban Watercourses

**Gary Beasley & Pauline Kneale**

**CONTENTS**

## LIST OF FIGURES



## LIST OF TABLES

## ABSTRACT

Good quality stream water and sediments are crucial for the support of healthy stream flora and fauna but urban runoff degrades watercourses leaving a legacy of pollution in the stream sediments. The sediment pollution load influences the development of macroinvertebrates which, as the lowest member of the food chain, influences the whole ecological structure. This review focuses on defining the sources and impacts of zinc, nickel, copper and oil derivative polycyclic aromatic hydrocarbon (PAH) contaminants in urban runoff. The impact of pollutants as measured by laboratory, field and modelling procedures are considered. Land use, position and connectivity of the runoff and sediment are seen to have an effect on the ecological integrity of the watercourse but case examples are sparse. The literature indicates that while reduced species diversity has been identified at a number of sites the dynamics are not well understood nor well modelled. These results are compared with field evidence from a study of 62 headwater streams with urban industrial and motorway land uses. From the review and field results it is evident that there is still an important need for process-based field measurements of urban water quality parameters. Forecasting the ecological status of watercourses would seem to benefit from data on sediment chemistry that considers the interaction effects of metals and PAHs.

## 1. BACKGROUND

Surface runoff in urban areas modifies and degrades stream water and sediments to the detriment of abstracted drinking water, recreational users and the aquatic and riparian ecology (Chandler, 1994; Ellis and Hvitved-Jacobsen, 1996). Concerns include the proliferation of toxic contaminants from point and non-point sources, but despite increased Government and public awareness, anthropogenic activities continue to impair watercourses (Karr and Chu, 2000; McCormick and Cairns, 1994; Moog and Chovanec, 2000). Improvement in the chemical quality of water in the UK and elsewhere has been achieved through large-scale curtailment of point source discharges and upgrading of combined sewer outflows, but these mitigation measures have highlighted the impact of non-point source pollution particularly storm water runoff from urban structures: pavements, streets, roofs, guttering and buildings ((Lazaro 1990; Malmqvist, 1983; Marsalek, 1990; Quek and Forster, 1993). This is of major concern for managers of freshwater ecology and considered the principal, critical, limiting factor in achieving ecological integrity in urban watercourses (Characklis and Wiesner, 1997; House *et al*., 1993; Lee and Bang, 2000; Lenat and Crawford, 1994; Pitt *et al*., 1995). Contamination of the water and the attachment of pollutants to streambed sediments impairs aquatic flora and fauna. Macroinvertebrates at the base of the food chain are particularly vulnerable and therefore can act as indicators of a river's biological health. In an effort to characterise more accurately the cumulative impact of human activities on ecosystems, monitoring is slowly moving away from reliance on chemical indicators towards use of ecological measures (McCormick and Cairns, 1994; Rochfort *et al*., 2000).

This review discusses the research available on the sources and impacts of three heavy metals and PAH contamination on macroinvertebrate communities in streams. Copper, zinc, and nickel are critical micro-nutrients, but also the most commonly detected metals in urban runoff (Marsalek, 1990). The evidence available on their ecological impact in streams from laboratory and field research is patchy and partial. It has tended to focus on expected worst-case field sites and controlled studies. The review is used to place in context the results from a study that sampled non-point source contamination of sediments at 62 headwater stream sites with natural, residential and industrialised catchment land uses. Heavy metal and oil contamination and the concomitant impairment of stream ecology is measured through BMWP scores and compared with RIVPACS forecasts for clean streams (Wright, 2000). Recommendations for further research concludes the discussion.

## 2. RIVER WATER QUALITY AUDITING

Control of contaminant discharges to aquatic environments began with the 1974 Paris Convention on the Prevention of Marine Pollution from Land Based Sources. The intention was to eliminate pollution by 'Black List' substances and to strictly limit 'Grey List' pollution. These were integrated into European legislation through the Council Framework Directive 76/464/EEC in 1976. The 131 contaminants on the Black List were considered to be of significant toxicity, persistent and capable of bioaccumulation in aquatic environments. The EEC sought to set limit values or emission standards (the latter set by reference to Environmental Quality Objectives, EQOs) for Black List substances at the Community level, and to promulgate daughter Directives on individual substances (Phillips and Rainbow, 1993). Contaminants on the Grey List were considered to exert deleterious impacts on aquatic environments, but it was thought that these could be confined to specific areas (of local, not regional or global concern). National control of Grey List substances operates through the setting of national emission standards designed to meet EQOs, not through community-wide limits. Further UK legislation includes the Water Act 1989, the Environmental Protection Act 1990 and the establishment of Statutory Water Quality Objectives (SWQOs). In the USA toxicants of aquatic concern total 126 and are recorded on the Priority Pollutants List.

Current water quality auditing in the UK by the Environment Agency (EA) is based on two interrelated functions originating from the National Water Council (NWC) classification system established in 1977. The EA (1997) use a General Quality Assessment (GQA) system for defining water quality and set a range of use-related Statutory Water Quality Objectives (SWQOs). The GQA defines quality for several components or 'windows' including chemical, biological, nutrient and aesthetic status. To date, only the chemical and biological components are established with greater emphasis placed on chemical status (Faulkner *et al*., 2000). Limitations of the current audit arise from the original NWC system where only three chemical determinants, biological oxygen demand, dissolved oxygen and ammonia are routinely monitored. There is no biological grade separation for example in terms of Biological Monitoring Working Party (BMWP) score or Average Score Per Taxon (ASPT). Using the River InVertebrate Prediction and Classification System (RIVPACS) (Wright *et al*., 1993a; 1993b), predict BMWP and ASPT scores for pristine watercourses and observed and predicted values are compared to produce an Ecosystem Quality Index (EQI) for selected reaches. The intention in the future is that the EQI will be used to develop a range of SWQOs for different uses of the watercourse. In the UK the River Ecosystem SWQOs is based on water column chemical rather than stream sediment chemistry audits.

Benthic macroinvertebrates live within the upper layers of streambed sediments in constant direct contact with contaminants, receiving prolonged exposure via cell osmosis and ingestion. This makes them excellent biomonitors of the ecological condition of a watercourse and as will be argued here monitoring sediment quality is potentially more consistent and valuable than monitoring water column chemistry

## 3. URBAN RUNOFF

There is considerable evidence that important sources of diffuse-source toxicants are related to heavily trafficked roads, industrial processes and storage areas. Vehicle-related sources affect the quality and quantity of road dust particles and pollutant residuals through petrol and oil spills, deposition of exhaust products and wear of tyre, brake and paving materials. Urban landscaping produces vegetation cuttings, fertilizer and pesticide residues in runoff, and the re-suspension and deposition of atmospheric pollutants adds to the pollutant load (Bannerman *et al*., 1993; Marsalek *et al*., 1999; Pitt *et al*., 1995). Pollutants include oil products, phenolic compounds, cyanide, arsenic, heavy metals (lead, zinc, copper, nickel, chromium, cadmium and mercury), chlorinated hydrocarbons, nitrates, sulphates, rubber, bitumen, glass, aggregate, tarmac derivatives and particles, derivatives from shoes, de-icing salt and spills from any type of transported load, animal wastes and everyday litter (Haslam, 1990). But example determinations of the full range of effluents in polluted water courses are rare.

Arguably, road runoff is the principal pollution source with heavily trafficked catchments producing more pollutants than lightly trafficked catchments (Andoh, 1994; Marsalek *et al*., 1999). Road-vehicle related pollutants include oil and tar products, dioxins, oxygenated compounds, halogenated phenols, metals, hydrocarbons, de-icing salts, and asbestos. Road runoff therefore contains a complex mixture of potential toxicants that can be transported untreated into receiving waters (Table

1). Surface roughness, vegetative cover, gradient, hydraulic connections to a drainage system, rainfall intensities, duration, antecedent dry period, pollutant availability and the natural and regional sources of pollutants may also be significant variables. The relative importance of the different source areas is therefore a function of catchment characteristics, pollutant wash off, and rainfall characteristics. Relatively few studies have described the fate of these contaminants, or have assessed the effect of road runoff on fresh water communities.

In this study 62 headwater sampling sites were selected in the Yorkshire region to consider the wider picture (Figure 1). Macroinvertebrates, heavy metals, water column chemistry variables, PAHs and physical environmental variables were sampled using standard methods and those used by the Environment Agency for RIVPACS forecasts to allow comparability with other studies. Sites were selected on different land use types rather than examining a specific 'probable worst case land use'. Samples were taken on residential, industrial and motorway sub-catchments. Where possible, samples were taken 25 m above and below a storm water inflow, and in sequence through residential and industrial areas. Amongst the sites were some that received runoff from motorways and road junctions. A sequential extraction technique was applied to the silt and sand fractions to determine the

**Table 1 Sources of heavy metals in pavement runoff, ** Primary Source, * Secondary Source (after Sansalone and Buchberger, 1997).**

| | **VEHICLES** | | | | **PAVEMENT** | | **SURFACE DEBRIS** | |
|---|---|---|---|---|---|---|---|---|
| | Brakes | Tyres | Frame and Body | Fuels and Oils | Concrete | Asphalt | De-icing Salts | Litter |
| Cadmium | * | ** | | | | | | |
| Chromium | | ** | | | | | | |
| Copper | ** | ** | | | | | | |
| Iron | | ** | ** | | | | | ** |
| Lead | * | * | | * | | | * | |
| Nickel | | ** | | | | | | |
| Vanadium | | | | ** | | | | |
| Zinc | ** | ** | ** | | | | | |
| Chlorides | | | | | | | ** | |
| Organic Solids | | | | | | ** | | ** |
| Inorganic Solids | | | * | | * | ** | | ** |
| PAHs | | | | * | | ** | | |
| Phenols | | | | | | ** | | |

importance of particle size and geochemical phases which heavy metals preferentially adhere to. In the Figures 2-8 the sites are ordered subjectively from those hypothesised to be the cleanest to those likely to be polluted, but within this ordering there is considerable noise because all sites on the same stream are plotted together. Identification of the most important contaminants in terms of their influence on macroinvertebrate community compositions was achieved using partial canonical correlation analysis (pCCA).

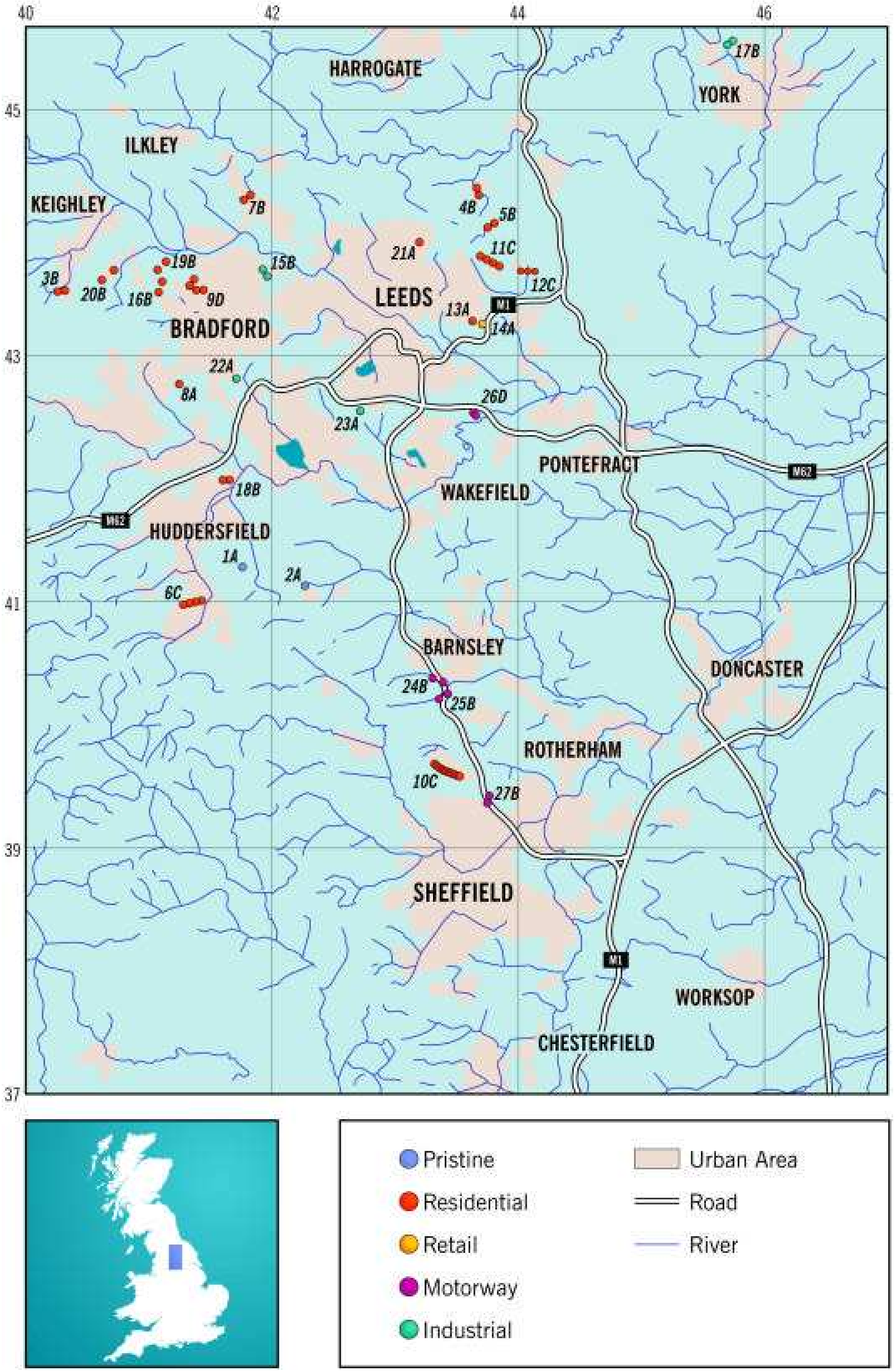
## 4. CONTAMINATED SEDIMENTS

Urban runoff entrains sediments that accumulate on surfaces between runoff events (Estèbe *et al*., 1997). Data from the USA indicated that urban runoff contained 250 - 300 mg $l^{1}$ of suspended sediment (Haughton and Hunter, 1994). Upon reaching the receiving water body the majority of the sediment settles out. This accumulation of contaminated streambed sediments is the principal underlying reason for reduced biointegrity for reasons well summarised by Power and 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 concentrations 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 area for many aquatic organisms.

Short term inputs of suspended sediment from construction sites have been shown to reduce the abundance of fish and invertebrates during and after construction (Ogbeibu and Victor, 1989). In Ontario, Taylor and Roff (1986) showed road construction runoff led to noticeable reductions in the abundance of species downstream for six years. So impacts may be long-lived. The time scale of the impact depends on many factors including the scale of

**Figure 1: Location of sampling stations in relation to major urban areas.**


40
42
44
46
45
43
41
39
37
HARROGATE
YORK
ILKLEY
KEIGHLEY
LEEDS
BRADFORD
PONTEFRACT
WAKEFIELD
HUDDERSFIELD
BARNSLEY
DONCASTER
ROTHERHAM
SHEFFIELD
WORKSOP
CHESTERFIELD
M1
M62
17B
7B
4B
5B
11C
12C
21A
19B
15B
3B
20B
16B
9D
13A
14A
22A
8A
23A
26D
18B
1A
2A
6C
24B
25B
10C
27B
Pristine
Residential
Retail
Motorway
Industrial
Urban Area
Road
River

construction, soil, climate, the size of receiving water body, the hydrological pathways linking the construction area with the receiving watercourse and the historic record of sedimentation and contamination in the catchment. (Catallo and Gambrell, 1987; Salomons *et al*., 1987; Wilber and Hunter, 1977).

## 5. MACROINVERTEBRATES AS QUALITY INDICATORS

Macroinvertebrates in streambed sediments are in constant contact with contaminants, receiving prolonged exposure via gill cell osmosis and ingestion, so assemblages adapt to the physical, chemical and ecological characteristics of their habitat (Cook, 1976; Griffiths, 1991; McCall and Soster, 1990; Milbrink, 1983; Plante and Downing, 1989). Their feeding facilitates the microbial degradation of the particulate organic matter and they are an important food resource for littoral and pelagic fish and birds (Amyot *et al*., 1994; Ciborowski and Corkum, 1988; Dermott and Lum, 1986; Katalin, 1988). Reduced macroinvertebrate diversity produces a negative feedback reducing overall ecological diversity (Ankley *et al*., 1992; Giesy *et al*., 1988). Because of their wide variation in sensitivity to contaminants, the presence or absence of sensitive or tolerant groups within communities make them excellent biomonitors of urban runoff pollution, relating sediment chemistry with biological quality. They possess advantages over fish as biomonitors as Metcalfe (1989) suggests:

- Benthic macroinvertebrate are ubiquitous, abundant and relatively easy to collect.
- They have long enough life spans to provide a record of environmental conditions.
- They are relatively sedentary and thus representative of local conditions.
- They are differentially sensitive to pollutants of various types and consequently are capable of a graded response to a broad range of kinds and degrees of stress.

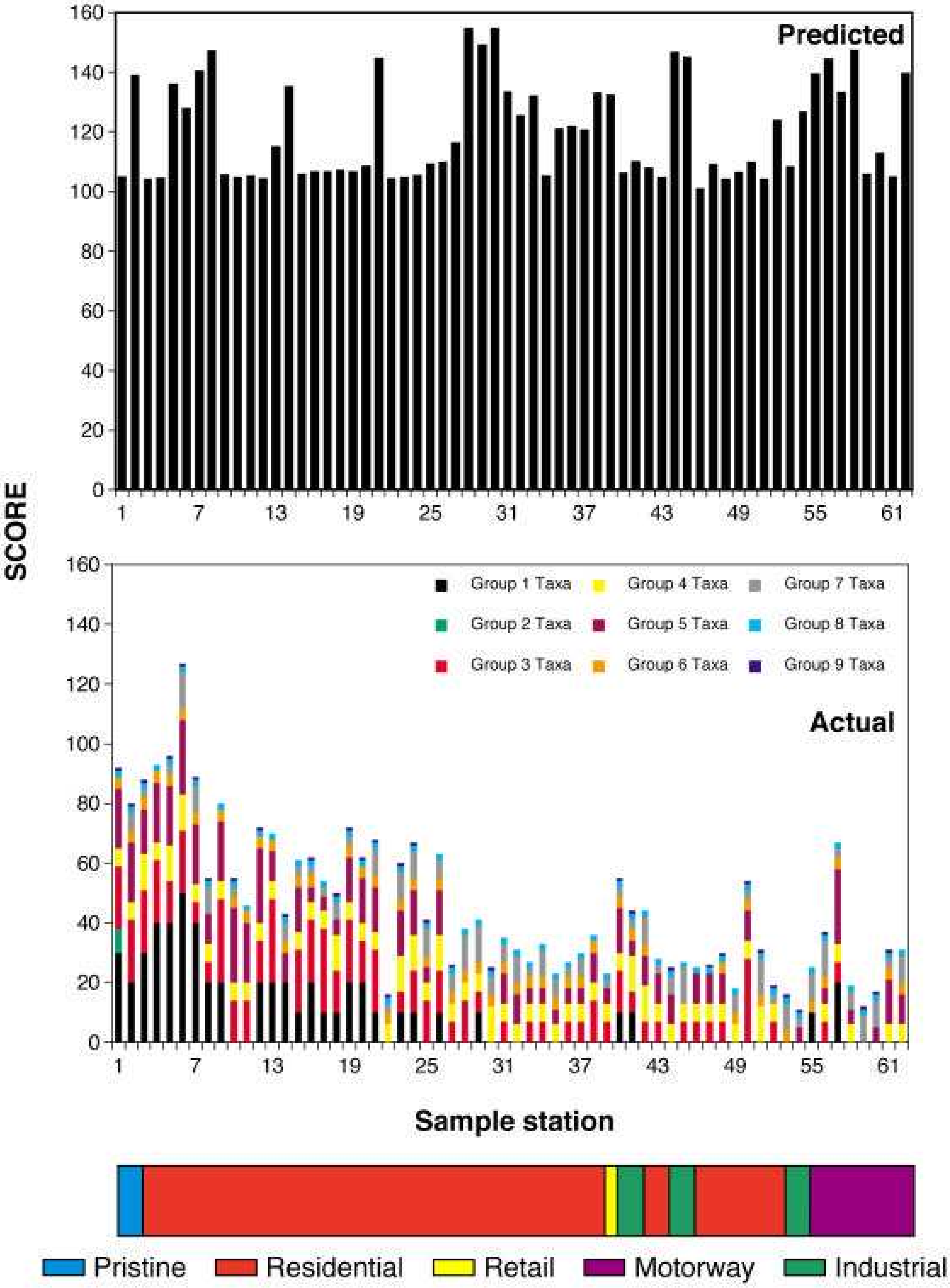
The GQA quality monitoring scheme presents some problems, especially since it ignores many of the most toxic substances such as heavy metals and hydrocarbons. Discrepancies between chemical and biological grades of water quality are common because of the difference in auditing practice. Snapshot chemical auditing represents conditions at the particular time of sampling and may imply a higher grade of water than biological monitoring would suggest. Macroinvertebrates represent a time-integrated tool, indicating the relatively long-term status of the watercourse. Ideally a water quality index should include those determinants which are increasing in the environment and those with the greatest deleterious impact on stream ecology.

Macroinvertebrate distribution at the 62 Yorkshire sites (Figure 2) indicate a decline in species numbers and diversity with land use change. Applying the RIVPACS model (Wright 2000) forecasts higher quality and more diverse ecological communities at all the sites. The total numbers and diversity decline as the catchments are more trafficked.

## 6. INORGANIC CHEMICALS

Since all metals are part of the earth's crust, distinction must be made as to whether the metals originate from natural or anthropogenic sources. Haughton and Hunter (1994) propose that domestic and industrial waste waters and sewage sludge are the principle sources, whereas Novotny (1995) states that urban and industrial non-point sources are the primary

**Figure 2: RIVPACS forecast and actual BMWP scores for all sampling stations, May 1999**


Predicted
Actual
SCORE
Sample station
Group 1 Taxa
Group 2 Taxa
Group 3 Taxa
Group 4 Taxa
Group 5 Taxa
Group 6 Taxa
Group 7 Taxa
Group 8 Taxa
Group 9 Taxa
0
20
40
60
80
100
120
140
160
1
7
13
19
25
31
37
43
49
55
61
Pristine
Residential
Retail
Motorway
Industrial

cause of pollution by toxic metals. Within urban areas metals originate from vehicles; corrosion, brakes, tyres, emissions and the deterioration (Table 2). A switch from metals such as nickel and chromium to plastics could help to curtail pollution.

**Table 2: Summary of inorganic contaminant sources in urban runoff (Makepeace *et al*., 1995).**

| **Element** | **Reported range ($mg\ l^{-1}$)** | **Typical sources** |
|---|---|---|
| Arsenic | 0.001 to 0.21 | Industrial emissions, fossil fuel combustion, smelting, laundry products, pesticides, weed killers, defoliants, preservatives. |
| Cadmium | 0.00005 to 13.75 | Combustion, wear of tyres and brake pads, combustion of lubricating oils, metal-finishing industrial emissions, agricultural use of sludge, fertilisers and pesticides, and corrosion of galvanised metals. |
| Copper | 0.00006 to 1.41 | Wear of tyres and brake linings, combustion of lubricating oils, corrosion of building materials, wear of moving parts in engines, smelter activity, metallurgical and other industrial emissions, algicides, fungicides, pesticides. |
| Lead | 0.00057 to 26.00 | Emissions from gasoline-powered vehicles, gasoline additives. |
| Nickel | 0.001 to 49.00 | Corrosion of welded metal plating, wear of moving parts in engines, electroplating and alloy manufacturing, activity of smelters, food production. |
| Zinc | 0.0007 to 22.00 | Wear from tyres, brake pads, combustion of lubrication oils, activity of smelters, corrosion of building materials and metal objects. |

Other significant sources of pollution by metals in urban areas include metallic roofs, gutters and downspouts, metallic corrugated pipes, old lead pipes, storage areas, parking lots, scrap yards and landfill sites. A comprehensive study of 150 surface and CSO runoff samples by Pitt and Barron (1989) showed CSO sites had the highest toxicities, followed by samples from parking and storage area runoff (Table 3).

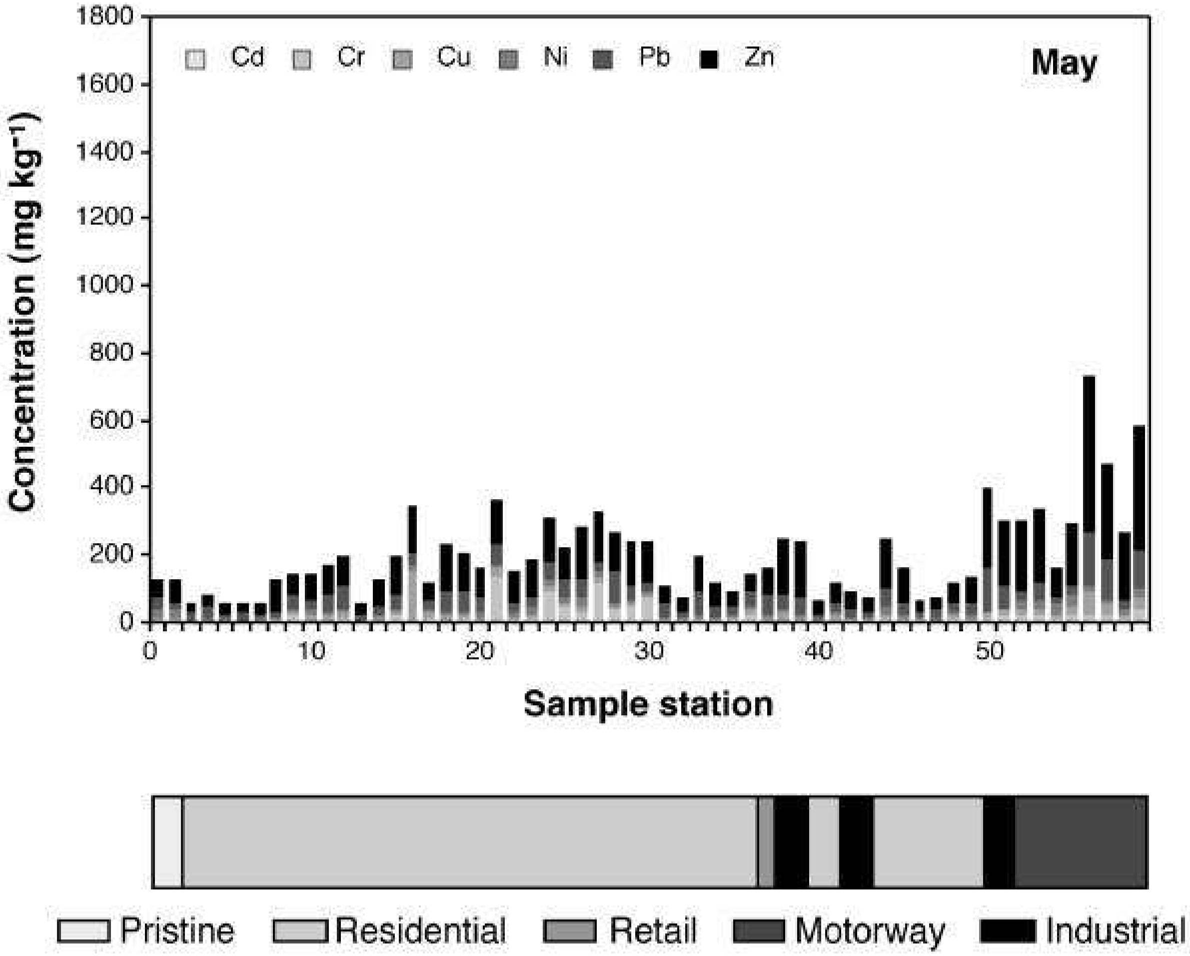
**Table 3: Concentrations of priority pollutants in runoff from urban source areas (Pitt and Barron, 1989: In Novotny, 1995).**

| **Constituent ($\mu g\ l^{-1}$)** | **Source areas** | | | | | |
|---|---|---|---|---|---|---|
| | Roofs | Parking | Storage | Streets | Vehicle service area | Landscaped area |
| Cadmium | 0.8 –30 | 0.7 – 70 | 2.4 – 10 | 0.7 - 220 | 8 - 30 | 0.04 – 1 |
| Chromium | 7 – 510 | 18 – 310 | 60 – 340 | 3.3 - 30 | 19 - 320 | 100 – 250 |
| Copper | 17 – 900 | 20 – 770 | 30 – 300 | 15 – 1250 | 8.3 - 580 | 80 – 300 |
| Lead | 13 – 170 | 30 – 130 | 30 – 330 | 30 - 150 | 75 - 110 | 9.4 – 70 |
| Nickel | 5 –70 | 40 – 130 | 30 – 90 | 3 – 70 | 35 - 70 | 30 – 130 |
| Zinc | 100- 1580 | 30 –150 | 66 – 290 | 58 - 130 | 67 - 130 | 32 – 1160 |

The principal concerns about heavy metals are their persistency in the environment as they do not generally degrade, volatilize or decay by photolysis (Novotny, 1995), and their ability to become concentrated in living tissue (bioaccumulation) thus threatening predators at the head of the food chain. As well as ultimately causing the death of aquatic organisms, some metals exert sub-lethal effects on aquatic organisms and predators such as birds and mammals, adversely affecting reproduction and behaviour (Beyer *et al*., 2000).

There are real comparability issues in the different measurement and presentation scales used by various authors to present their data. Figure 3 reports total heavy metal concentrations at the Yorkshire sites. Increasing concentrations are seen as expected as sites become more affected by urbanisation, but total metal concentrations are of limited value in ecological studies. In looking at the impact on stream flora and fauna it is the available metals that are extracted during the first stage of analysis that are of interest. In the next section the bio-available metal results are the focus of the discussions.

**Figure 3 Total heavy metal concentrations for May 1999.**



## 6.1 Nickel

Nickel is one of five metals (copper, zinc, chromium and lead) in the top sixteen most commonly discharged priority pollutants on the EEC Grey List and the USA Priority Pollutants List. As well as at point sources, relatively high concentrations are present in urban surface runoff (Novotny, 1995; National Safety Council, 1997). Natural rock concentrations of 60 to 90 mg $kg^{-1}$ are increasingly complemented by anthropogenic sources associated with the production of over 3000 different alloys, electroplating, mining and smelting, household appliances, batteries, welding products, pulp and paper, and fossil fuel combustion emissions. These sources have been responsible for almost doubling the concentration of nickel in recipient freshwaters every decade since 1930 (Biney *et al.*, 1994; Sreedevi *et al.*, 1992). Of the 51.3 million kilograms of nickel emitted into the atmosphere world wide, 52 percent originates from residential and fuel oil consumption; 14 percent from mining and refining operations; 10 percent from incineration; 9.3 percent from naturally windblown dust and 4.9 percent from volcanoes (National Safety Council, 1997).

The predominant oxidation state in natural waters is $Ni^{++}$ within the pH range 5 to 9. Nickel, like ferrous metals, has a high electronegativity and as such has a high affinity to clay minerals. Adsorption to clay minerals means that concentrations in sediments are several orders of magnitude greater than in the overlying water column (Stokes, 1988). Nickel also occurs as soluble salts and organic complexes. However, difficulties in quantifying the fraction of nickel present as organic complexes and knowledge that adsorbed metal is not, a *priori*, readily available for toxicological processes means water quality criteria are based on total soluble nickel (Biney *et al.*, 1994).

Nickel was initially considered to have no essential biological function, but research since 1975 indicates that nickel is significantly involved in plant, animal and bacterial systems (Boyle and

Robinson, 1988). Plant physiologists showed that nickel was a constituent of urease and absolute requirements of the element were discovered to be widespread in marine microalgae (Stokes, 1988). There is as yet no determination of the absolute requirements for nickel in fresh water algae, or other aquatic organisms. But nickel, though essential in trace quantities, is highly harmful to the survival and productivity of aquatic fauna. In higher concentrations it affects populations of commercially important marine and fresh water food fishes, and consumption of nickel contaminated fish by humans may cause a number of disorders (Chaudhry and Kedarnath, 1985; Moore and Ramamoorthy, 1984).

Low pH and the presence of chloride, nitrate, sulphate, and soluble (colloidal) humic matter promote the migration of nickel in natural waters. Factors that limit the migration of nickel are high pH and the presence of $PO_4^{3-}$, $CO_3^{2-}$, $OH^-$, and $H_2S$, which precipitate the metal as insoluble salts. The presence of organic (chelating) substances, humus, hydroxides of iron, manganese, aluminium, and silica-alumina complexes (clay minerals) remove nickel from the water column by absorbance and adsorption.

Nickel concentrations within sediments vary depending on the type of geological terrain and on the presence of nickeliferous rocks and deposits, proximity of nickel smelters, electroplating plants, industrial and domestic contamination including transport emissions. Boyle and Robinson (1988) disclosed a hierarchy in which streams sediments commonly possessed a greater nickel content than river and lake sediments consequent of receiving the 'first flush' of pollution, greater wetted perimeter and less dilution. Typically concentrations lie between 1 to 150 ppm for uncontaminated sites rising by 3 to 10 fold in the presence of nickeliferous rocks and deposits. Concentrations of nickel (measured as total nickel) in UK rivers ranges from 0.0007 to 0.0037 mg $l^{-1}$ for clean and from 0.012 to 0.073 mg $l^{-1}$ for polluted waters (EIFAC, 1984; Biney *et al.*, 1994). Boyle and Robinson (1988) quoted similar values of 0.0005 to 0.02 mg $l^{-1}$ (Table 4). Concentrations in North American fresh waters have been reported to be slightly greater at 0.003 to 0.017 mg $l^{-1}$ (Biney *et al.*, 1994; Jenkins, 1980).

**Table 4 Average or range of nickel concentrations in natural waters (Boyle and Robinson, 1988).**

| Description | Ni content (mg $l^{-1}$) |
|---|---|
| Rainwater and snow (mostly in particulate matter) | Up to 0.001 |
| Hot springs | 0.0005-0.4 |
| Groundwaters and cold springs | 0.0005-4.5 |
| Groundwaters, cold springs, and mine waters in vicinity of nickeliferous deposits | Up to 75 |
| Stream, river, and lake waters | 0.0005-0.02 |
| Natural stream and river waters in vicinity of nickeliferous deposits | Up to 5 |
| Contaminated stream, river, and lake waters in vicinity of nickel mines and smelters | Up to 6.4 |
| Ocean and seawaters | 0.0015 |
| Normal Fe-Mn precipitates (dry matter) from springs | 7-100 |
| Fe-Mn precipitates (dry matter) from springs in vicinity of nickeliferous deposits | 20-2000+ |
| Stream and river sediments (dry matter) | 1-150 |
| Natural stream and river sediments (dry matter) in vicinity of nickeliferous deposits | Up to 1000 |
| Contaminated stream, river, and lake sediments (dry matter) in vicinity of nickel-mining areas | Up to 3000 |

Studies of nickel toxicity to macroinvertebrates are too scarce to assess properly the influence of environmental factors on toxicity (Biney *et al.*, 1994). Stokes (1988) identified Oligochaetes and Crustaceans as displaying the greatest degree of sensitivity (Table 5). He suggested that benthic organisms are likely to display a greater tolerance than planktonic organisms in the same system as higher nickel concentrations are associated with sediments. However, sub-lethal responses to the presence of nickel such as changes in the growth rate, enzyme activity and reproductive rate have been reported, but again data are limited. There seem to be no studies that show the mechanisms of nickel toxicity in macroinvertebrates.

**Table 5 Effect of nickel on selected macroinvertebrates (Stokes, 1988).**

| Organism | Conditions | Test | Nickel concentration causing toxicity (mg $l^{-1}$) |
|---|---|---|---|
| *Daphnia magna* (fresh water cladoceran) | 18°C 45mg $l^{-1}$ | $LC_{50}$ | <0.32 |
| *Asellus aquaticus* (fresh water isopod) | Soft water | $LC_{50}$ 48hr | 435 |
| *Crangonyx pseudogracilis* (fresh water amphipod) | Soft water | $LC_{50}$ 48hr | 252 |
| *Chironomus* (fresh water midge larvae) | Freshwater | $LC_{50}$ 48hr | 79-169 |
| *Clistoronia magnificans* (caddisfly) | Freshwater | Life cycle prevented from completion | 0.25 |
| *Juga plicifera* (fresh water snail) | Freshwater | $LC_{50}$ 96hr | 0.237 |
| *Allorchestes compressa* (marine amphipod) | Saltwater | $LC_{50}$ 96hr | 35 |
| *Macoma balthica* (marine deposit feeder) | Saltwater | $LC_{50}$ | 5-54 |

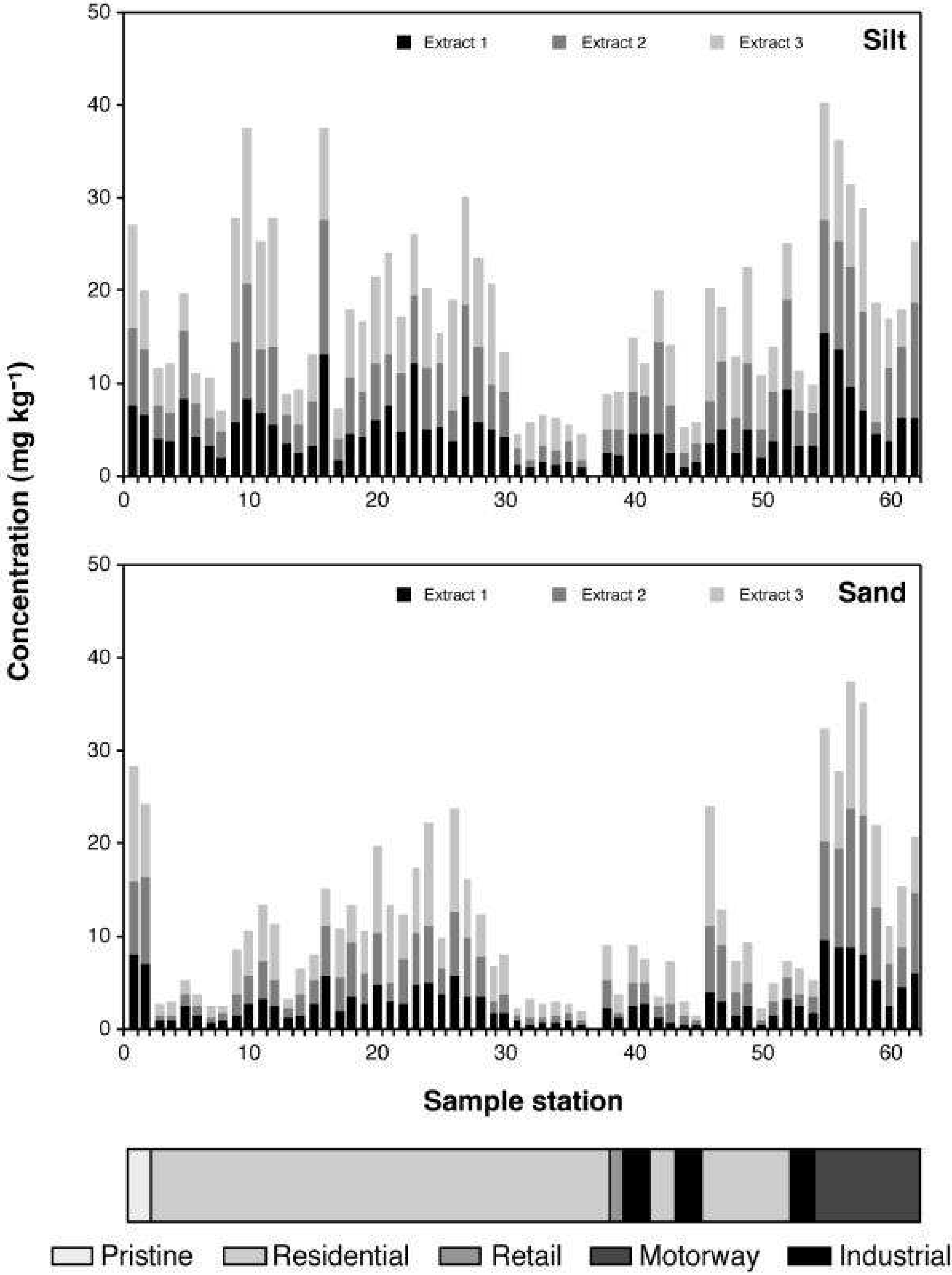
At the Yorkshire sites (Figure 4) nickel tends to show an equal affinity to both silt and sand fractions with only marginally lower values observed in sand. Unlike cadmium, chromium and copper at these sites, the percentage in each extraction phase is similar (28%, 32% and 40% for extracts 1, 2 and 3). Unlike the other metal results in this study, total nickel contamination is also high at the pristine upstream reference sites. So although from Figure 4 it would appear that those stations receiving motorway drainage are relatively heavily contaminated with nickel so too are their upstream stations. Contamination at the upstream motorway stations may have a vehicular source or may be due to natural lithological enrichment. What is perhaps easier to establish is the pattern of stations recording low concentrations. The most interesting fact is that stations 31-37 on two adjacent stream systems have low values, supporting the inference of natural lithological controls. Both stream systems are located on the northern edge of the coal measures and Sherwood sandstone. However the highest values are found at the sites with significant road runoff from the motorway and industrial areas and sites with on-street parking and denser road networks.

### 6.2 Copper

The average concentration of copper in the earth's crust is 4.5 mg $kg^{-1}$ and is widely distributed as sulphides, oxides, carbonates, arsenides and chlorides. Copper deposits occur as the ore chalcopyrite ($CuFeS_2$), cuprite ($Cu_2O$), chalcocite ($Cu_2S$) and malachite $Cu_2CO_3(OH)_2$

(Mance *et al*., 1984). World consumption is approximately 8 million tonnes, of which the UK consumes 330000 tonnes and Europe 2.2 million tonnes. Copper is widely used in the manufacture of alloys with zinc, nickel and tin, in metal plating and in the production of copper wire and piping. Compounds of copper are used in a variety of manufacturing

**Figure 4 Concentrations of nickel in silt (<63µm) and sand (>63µm) for each sequential extraction phase, May 1999.**



Silt
Extract 1
Extract 2
Extract 3
Sand
Concentration (mg kg⁻¹)
Sample station
Pristine
Residential
Retail
Motorway
Industrial

industries: copper nitrate in plating and textile dyeing processes; copper chloride in the manufacture of glass and ceramics and as a catalyst in the production of vinyl chloride. Copper compounds including cuprous oxide, cupric sulphate and cupric acetate are used as fungicides, in the manufacture of wood preserving agents, rayon and paint pigments. In products such as wire, piping and plated metal copper is generally immobilised, although some release can occur, for example, from water heating systems. Copper from fungicide products may also find its way into the aquatic environment. Using copper sulphate as an algicide can result in its direct addition to water supply reservoirs (Mance *et al*., 1984).

Copper is also an essential nutrient and is therefore present in human and animal wastes.
Copper may exist in a natural water system either in the dissolved form as the cupric ion or complexed with inorganic ions or organic ligands such as carbonates, chlorides, humic and fulvic acids, or as suspended sediment when present as precipitates (e.g. hydroxides, phosphates, sulphides) or adsorbed by particulate matter. Alternatively it can be adsorbed to sediments or exist as settled precipitates. The concentration of each of these forms depends on the complex interaction of variables including the concentration of copper, hardness, alkalinity, salinity, pH, concentration of bicarbonate, carbonate, sulphide, phosphate, organic ligands and with other metal ions competing for ligands and adsorption sites.

In fresh waters, in the absence of organic ligands, hydrolysis and precipitation are the most important processes influencing the oxidation chemistry and determining the predominant copper species; expected to be $Cu^{++}$ below pH 6 and carbonate complexes between pH 6 and 9.3. At the pH values of most aerated fresh waters, basic copper carbonate and cupric hydroxide precipitate out of solution or form colloidal suspension at concentrations greater than about 0.5 mg Cu $l^{-1}$. The presence of humic acids, fulvic acids, and detergents alter this equilibrium such that most of the copper becomes organically complexed.

The capacity of river waters to remove copper from solution may be greater than lake waters because of the larger amounts of particulate matter in suspension. The fate of copper associated with the particulate matter is influenced by several factors. Copper introduced into river systems from municipal and industrial discharges is often incorporated into sediments near the sources. However, intermittent high stream flows which re-suspend sediments and change local water chemistry may lead to the re-mobilization of copper. For instance a change from anaerobic to aerobic conditions, a decrease in pH or the presence of complexing agents could all release copper into the overlying water. The proportion of copper associated with particulate matter transported in rivers may range between 20 and 90 percent (Mance *et al*., 1984).

The toxicity of copper to freshwater invertebrates has been most recently reviewed by Mance *et al*. (1984). The available information for acute and chronic toxicity is summarized in Tables 6 and 7. From these results and others using microcosms, higher concentrations have been found to be acceptable in areas where a history of copper contamination has allowed acclimatization (Courtney and Clements, 2000), or where the presence of organic materials leads to complexation of the copper.

**Table 6 The short-term lethal tolerance of freshwater macroinvertebrates to copper (Mance *et al*., 1984).**

| **Organism** | **Duration** | **Hardness (mg $l^{-1}$ Ca $CO_3$)** | **LC50 (mg $l^{-1}$)** |
|---|---|---|---|
| **OLIGOCHAETA** | | | |
| *Limnodrilus hoffmeisteri* | 96h | 100 | 0.100 |
| **INSECTA** | | | |
| *Acroneuria lycorias* | 96h | 44 | 8.3 |
| *Ephemerella subvaria* | 96h | 44 | 0.32 |
| **ROTIFERA** | | | |
| *Philodina acuticornis* | 96h | 25 | 0.7 |
| *Philodina acuticornis* | 96h | 81 | 1.1 |
| **GASTPROPODA** | | | |
| *Biomphalaria glabrata* | 24h | | 3.2 |
| *Campeloma decisum* | 96h | 45 | 1.7 |
| *Physa integra* | 96h | 45 | 0.039 |
| *Physa sp.* | | (25?) | 0.035* |
| *Physa sp.* | | (160?) | 0.083* |
| *Gyraulus circumstriatus* | | 100 | 0.11* |
| *Physa heterotropha* (pre-adult) | | 20 | 0.016* |
| *Physa heterotropha* (pre-adult) | | 100 | 0.013* |
| *Physa heterotropha* (adults) | | 100 | 0.069* |
| *Goniobasis livescens* | 48h | 150 | 0.86 |
| *Lymnaea emarginata* | 48h | 150 | 0.3 |
| **CRUSTACEA** | | | |
| *Gammarus pseudolimnaeus* | 96h | 45 | 0.02 |
| *Daphnia magna* | 48h | 45 | 0.06 |
| *Daphnia magna* | 72h | 130 - 160 | 0.08 - 0.085 |
| *Daphnia pulex* | 72h | 130 - 160 | 0.086 |
| *Daphnia parvula* | 72h | 130 - 160 | 0.072 |
| *Daphnia ambigua* | 72h | 130 - 160 | 0.0677 |

*Exposure times less than 96h.

**Table 7 Chronic toxicity of copper to freshwater macroinvertebrates (Mance *et al*., 1984).**

| **Organism** | **Hardness (mg $l^{-1}$ as Ca $CO_3$)** | **Copper concentration ($\mu g\ l^{-1}$)** | **Effect** |
|---|---|---|---|
| *Daphnia* (4 spp.) | 130 - 160 | 60 | Longevity reduced 7 weeks |
| *Gammarus seudolimnaeus* | 44 | 28 | 100% mortality 6 weeks |
| *Gammarus seudolimnaeus* | 44 | 15 | |
| *Gammarus seudolimnaeus* | 44 | 8 | 100% mortality 15 weeks |
| *Physa integra* | 44 | 28 | 90% mortality 6 weeks |
| *Campeloma decisum* | 44 | 28 | 80% mortality 6 weeks |
| *Campeloma decisum* | 44 | 15 | 50% mortality 6 weeks |
| *Hydropsyche betteni* | 46 | 32000 | 14-d LC50 |

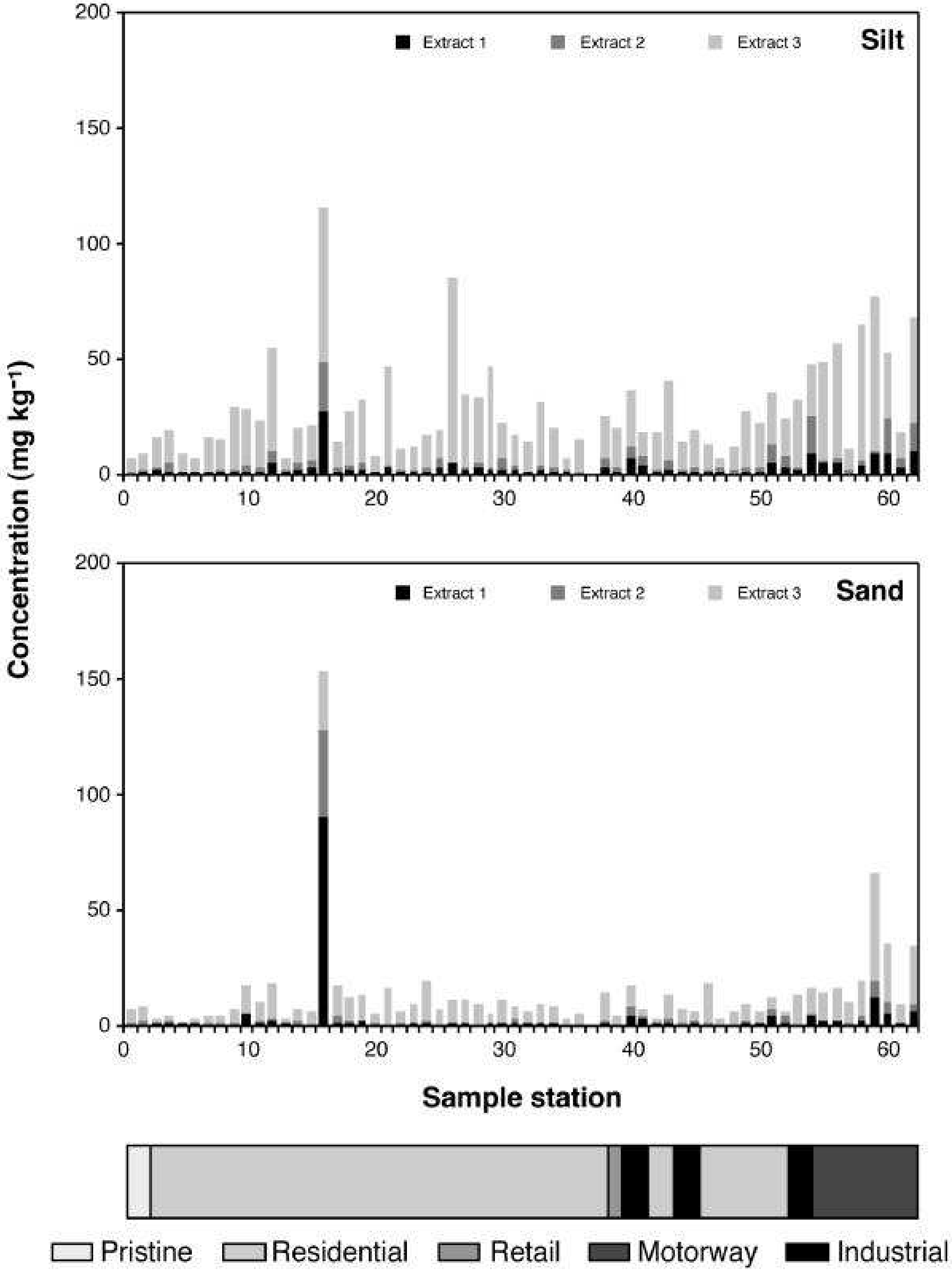
Leland *et al*. (1989) expressed concern over typical laboratory assays of metal toxicity to aquatic insects in that they tend to expose middle or late-instar stages from natural streams when they are in their intermoult status. They advocate testing during early developmental stages and periods of moult, which are times of exceptional stress and sensitivity instead. A heightened sensitivity to copper (5 or 10 $\mu g\ l^{-1}$ $Cu_T$) at early development stages was reflected in the different concentrations seen during autumn 1978 and 1979 effecting population declines of many benthic insects in their Convict Creek study. By initiating dosing earlier in 1979 than 1978, they observed a lack of early instars in the autumn. As with other aquatic insects little is known regarding the mechanism causing the sensitivity to metals, but it may be attributed to damage of respiratory membranes. Species size was a factor suggesting that some single species toxicity tests may identify higher metal tolerances through using larger specimens (Hickey and Clements, 1998). Declines in population density of species representing all major orders (Ephemeroptera, Plecoptera, Coleoptera, Trichoptera and Diptera) occurred at copper concentrations of 5 and 10$\mu$g $l^{-1}$ (Leland *et al*., 1989).

In the Yorkshire sampling (Figure 5) there is considerable station to station variability in copper. Most noticeable are the high values in both fractions and for all three extracts for station 16 in May. This was probably associated with road works on a major road above station 16 with regular braking leading to wear of tyre and brake pads. However the impacts of such short-term variations in catchment sediment chemistry requires further investigation.

Most of the copper is bound to the sediment until the third extraction. Only 10 percent of the total concentration is released in the first extract compared to approximately 75 percent released in extraction phase 3. For the majority of sampling stations this means low bioavailable concentrations, but for stations such as 54, 428.86 mg $kg^{-1}$ is available from the sand fraction.

Copper contamination appears to be related to the flow of vehicles and the road network characteristics. The variability in the data suggests strongly that high vehicle numbers on roads with moderate gradients and motorway exit lanes or roundabouts or junctions are associated with the highest copper values. The majority of sample stations are identified as having copper levels in silt which exceed levels at the control sites for all three extracts, and

**Figure 5 Concentrations of copper in silt (<63µm) and sand (>63µm) for each sequential extraction phase, May 1999.**



particularly extract 3. This was expected given that copper is a major component of vehicle brake pads and vehicles are common to all the study catchments

### 6.3 Zinc

Zinc is one of the most commonly used metals in the world (EBI, 1998). The global production of zinc increased steadily during the 20th century and almost doubled in the 1990s. The largest use is in galvanizing iron and steel products, brass products and zinc-based alloys. It is also used in synthetic rubber, paints, cosmetics, ceramics, manufacturing and dyeing of textiles, wood preserves and the purification of fats (Radhakrishnaiah *et al.*, 1993). Despite increasing use and release into the environment, there is a paucity of information concerning its aquatic chemistry. Most zinc enters the environment as a result of human activities, such as mining, purifying of zinc, lead and calcium ores, steel production, coal burning, burning of wastes and from municipal waste treatment discharges. Zinc though essential for certain biological functions in minute quantities, is highly toxic beyond these requirements. Many zinc salts are highly soluble in water and with half-lives greater than 200 days (EBI, 1998) they pose serious toxic threats to aquatic flora and fauna.

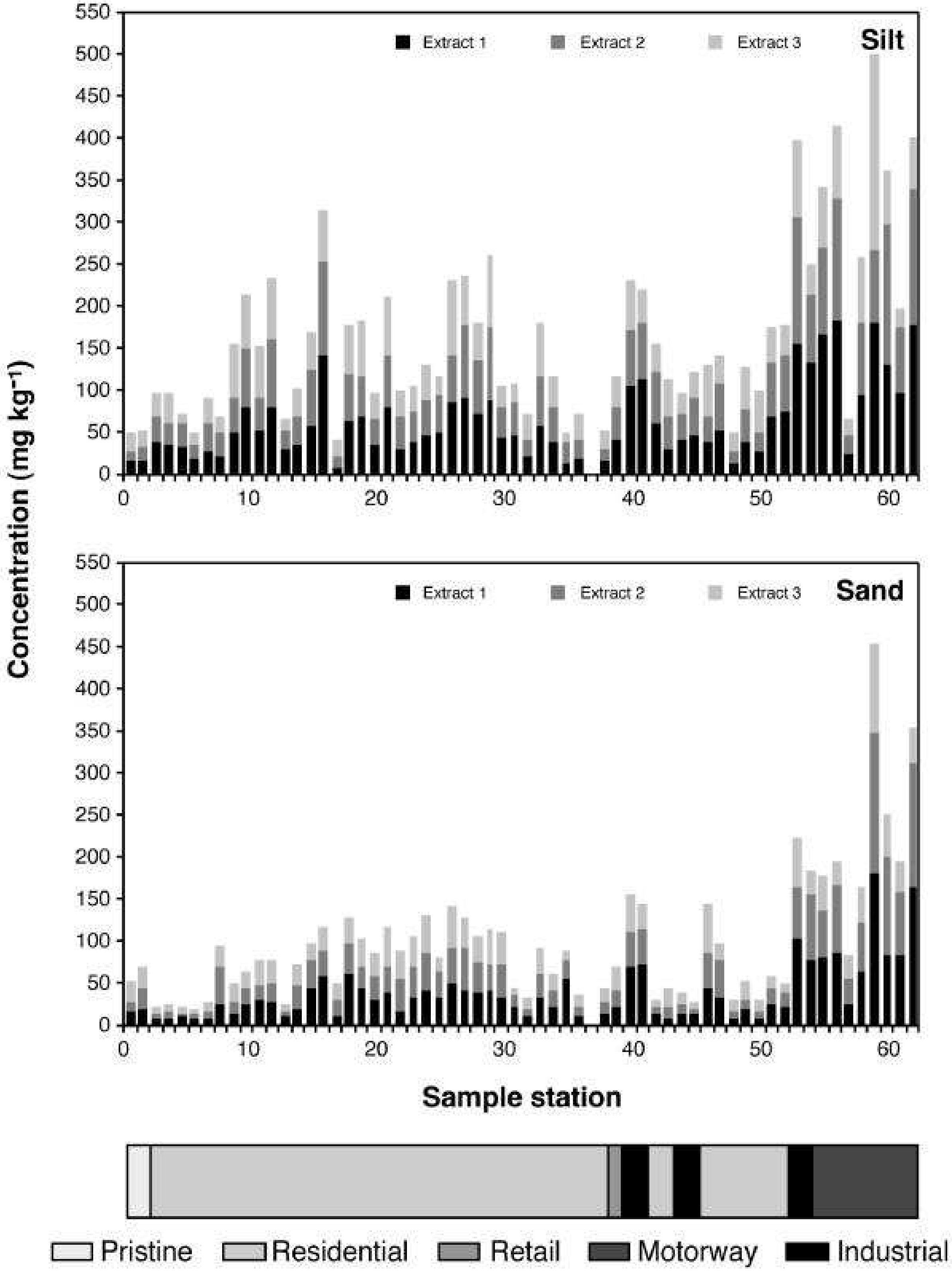
Maltby and Naylor (1990) used brooding female *Gammarus pulex* to compare the effect of zinc on Scope for Growth (SfG) and on reproduction. Brooding females were used to evaluate short-term stress changes in the energy budget, as measured by the SfG assay, which might relate to longer term effects on reproduction. Increased zinc concentrations produced a significant reduction in energy absorbed, but no change in respiratory loss that resulted in a significant reduction in SfG. The lowest concentration of zinc to be significantly different from the control was 0.3mg Zn $l^{-1}$.

Results demonstrated that brooding females were more sensitive than males. Zinc caused an increase in the number of broods aborted but there was no reduction in the number of offspring produced in either the present or subsequent broods. The authors suggested that the effect of zinc on the reproductive output of *Gammarus pulex* was to influence energy allocation rather than to kill broodlings or eggs. Such stress induced reductions in offspring size and brood viability could influence profoundly the population as a whole. Other things being equal, it has been found that smaller offspring take longer to mature (Sibly and Calow, 1985) and such animals may reproduce at a smaller size, which for both males and females, means reduced fecundity.

The pattern of zinc concentrations in the Yorkshire streams increases as sites become more urbanised. The proportion of total zinc extracted shows limited variability between size fractions (Figure 6). The percentage extracted is reduced slightly with progression from extracts 1 through to 3, which means that, as with cadmium in this study, the largest proportion of total zinc is released in the first extraction step. Almost 40% is bioavailable and susceptible to uptake by organisms.

The highest zinc contamination is associated with industrial and motorway land uses. As with copper, zinc is a major component of tyres and brake pads and so was expected to be highest where wear and tear of these vehicle parts is most likely to occur. This is substantiated by the fact that the highest concentrations occur, as with copper, at stations receiving runoff roundabouts, junctions and on exit roads. Contamination is severe at sample

**Figure 6 Concentrations of zinc in silt (<63μm) and sand (>63μm) for each sequential extraction phase, May 1999.**




station 16, most noticeably in the silt fraction, where there are high vehicle flows and a steep gradient on the busy 'A' road from which the runoff derives. Stations 9-12 and 20-30 have high zinc concentrations which is perhaps explained by the dense road networks of the adjacent housing estates, on street parking and possible historical industrial activity.

For silt extract 1, 73 percent of sample stations have zinc levels in excess of 200% of the control site values. This high percentage demonstrates the widespread spatial distribution of elevated zinc that includes all of the land uses studied. Those stations where exceptionally high values are recorded are, as expected, sub-catchments that contain major 'A' roads, industrial and motorway land use.

### 6.4 Tolerance to combinations of metals

More recently single metal and single species bioassays have been complemented by multispecies experiments using indigenous stream organisms and mixtures of metals tested in artificial stream microcosms (Courtney and Clements, 2000; Harrahy and Clements, 1997; Kiffney and Clements, 1994a, 1994b, 1996a, 1996b). Subjecting a natural assemblage to a mixture of cadmium, copper, and zinc at chronic criteria values, Kiffney and Clements (1994a) identified that the majority of Ephemeroptera (mayflies) and Plecoptera (stoneflies) species were sensitive to metal contamination. They found increased densities of *Chironomidae* and reduced densities of *Baetidae*, *Heptageniidae* and *Ephemerellidae* once exposed to the metal mixture (Table 8). Such results support the findings of Clements (1991b) and Clements and Rees (1997) who identified a tolerance continuum in the order Chironomids > Trichoptera > Plecoptera > Ephemeroptera. Nelson and Roline (1996) also

**Table 8 Relative change in abundance of dominant taxa, major insect groups, and community-level indices in 1 x treatment streams (*n* = 3) compared with control streams (*n* = 3), (Kiffney and Clements, 1994b).**

| Taxa | % change |
|---|---|
| Ephemeroptera | - 68 |
| *Heptageniidae* | - 90 |
| *Baetis tricaudatus* | - 76 |
| *Drunella grandis* | - 65 |
| *D. doddsi* | - 66 |
| Plecoptera | - 44 |
| *Pteronaecella badia* | - 60 |
| *Suwallia pallidula* | - 36 |
| *Sweltsa coloradensis* | 0 |
| Trichoptera | - 12 |
| *Lepidostoma ormeum* | - 17 |
| Chironomidae | + 56 |
| *Tanypodinae sp.* | + 94 |
| *Orthocladiinae sp.* | + 5 |
| *Chironomini sp.* | + 8 |
| *Tanytarsini sp.* | + 84 |
| Number of individuals | - 20 |
| Number of taxa | - 22 |

recognised that *Heptageniidae* could be a metal sensitive indicator species given its preference for metal free streams. Such tolerance is different at family and species level (Clements, 1991a). Differences to metal tolerance have also been related to a number of other factors such as altitude (Clements and Kiffney, 1995; Kiffney and Clements, 1996b), stream order (Kiffney and Clements, 1994b), stream metal histories (Courtney and Clements, 2000) and organism size (Kiffney and Clements, 1996a). In their study on altitude Kiffney and Clements (1996b) found that assemblages from small, high altitude streams were 12 – 85 percent more sensitive to metal pollution in comparison to those from larger, low altitude streams. Similarly with stream order, assemblages from 4$^{th}$ order streams were more tolerant than their 3$^{rd}$ order counterparts, as were assemblages from streams with a metal pollution history compared to those from a clean reference stream.

Some microcosm studies are validated with complementary field experiments. Hickney and Clements (1998) found good agreement between toxicity tests and measures of community structure in streams in New Zealand, especially at stations where elevated metal concentrations dominated other confounding factors. The New Zealand results were similar to those obtained in both North America and Europe, re-enforcing the idea that responses of macroinvertebrate assemblages to metal contamination are consistent and predictable.

In an attempt to identify principal toxicants many studies have focused on *in situ* bioassays, exposing single indicator species to a mixture of metals within the streams themselves. Mulliss *et al*. (1994, 1996a, 1996b) exposed caged *Asselids* and *Gammarus pulex* to a mixture of contaminants from a storm water overflow. Using Principal Components Analysis (PCA) they show that total aqueous copper affected both species mortality, and that total aqueous lead and dissolved copper and zinc affected the mortality of *Gammarus*. However, Maltby *et al*. (1995b) found that stream water contaminated with motorway runoff was not toxic to *Gammarus* whereas, exposure to contaminated sediments resulted in a reduction in survival rates over a 14 day exposure period. In this study the authors identified PAHs, copper and zinc as the major toxicants.

In a field study Van Hessel *et al*. (1980) observed elevated metal concentrations in sediments, macroinvertebrates and fish at stations receiving road runoff indicating the threat of roads as a major contaminant source. Shutes (1985) identified bioconcentration with higher tissue concentrations of lead, cadmium, copper and zinc in those macroinvertebrates inhabiting urbanised streams compared with a semi-rural stream (Table 10).

**Table 9 Mean metal concentrations in dry weight of samples ($\mu g\ g^{-1}$) (Shutes, 1985).**

| Organism | Station | Cadmium | Copper | Lead | Zinc |
|---|---|---|---|---|---|
| *Gammarus pulex* | 1.1a | Ndt | 48.4 | ndt | 114.4 |
| | 1.1 | 0.5 | 80.3 | ndt | 74.8 |
| | 1.3 | 0.6 | 79.4 | ndt | 74.8 |
| | 1.4 | 0.3 | 77.6 | ndt | 77.2 |
| | 1.6 | 1.3 | 102.8 | ndt | 98.4 |
| | 2.1 | 13.8 | 108.3 | 114.4 | 735.5 |
| | 2.2 | 2.0 | 126.3 | 187.2 | 607.7 |
| *Asellus aquaticus* | 2.2 | 43.3 | 115.9 | 233.5 | 313.0 |
| *Erpobdella octoculata* | 2.2 | Ndt | 151.3 | ndt | 626.6 |
| | 2.4 | 1.8 | 405.0 | 69.5 | 1246.4 |
| *Limnephilus sp*. | 2.1 | 2.3 | 49.0 | 174.4 | 741.7 |
| *Limnaea peregra* | 2.2 | 10.3 | 69.0 | 91.2 | 274.5 |
| | 2.3 | 11.2 | 75.3 | 56.7 | 169.3 |
| | 2.4 | 11.1 | 131.0 | 153.7 | 510.1 |
| | 2.5 | 8.8 | 335.4 | 134.2 | 355.7 |
| | 2.6 | 7.3 | 142.2 | 347.7 | 618.7 |

Lenat and Crawford (1994) studied three streams in the piedmont eco-region of North Carolina to evaluate the effect of land use (forested, agricultural, urban) on water quality and aquatic biota. The greatest sediment yield and highest concentrations of heavy metals (chromium, copper and lead) were in streams associated with urban land use. The fish community at the urban site showed reduced species richness, low biomass, and an abundance of metal-tolerant species. Macroinvertebrate taxa richness, and the number of unique species (found at only one site) indicated moderate stress (fair water quality) at the agricultural site and severe stress at the urban site. Taxa richness decreased significantly for nine taxonomic groups, increasing only for tolerant Oligochaeta.

Dominant macroinvertebrates groups shifted from Ephemeroptera at the forested site, to Chironomids at the agricultural site and Oligochaeta at the urban site (unique species at the urban stream were limited to the most tolerant groups: Oligochaeta, 55 percent and Diptera, 24 percent). The authors concluded that this pattern is typical of highly stressed streams.

Parallel community changes were found by Kemp and Spotila (1997) in Valley Creek, Pennsylvania, and by Whiting and Clifford (1983) who observed depressed macroinvertebrate diversity and species richness in an inner city stream in Alberta, Canada. Most noticeable was the loss of certain Ephemeroptera, Gammarus and Tricoptera taxa and their replacement within the assemblage by Oligachaetes and Chironomids. Examining residential runoff in Illinois, Casper (1994) found a subtle shift in community structure with a 76 percent reduction in the main predator *Salis* resulting from elevated metal concentrations in sediment. The result was a significant increase in population abundance of pollution tolerant prey.

A literature review by Goodyear and McNeill (1999) concluded that the relationships between zinc concentrations in sediments and in macroinvertebrates were significant for collector - gatherers, scraper – grazer and predators at the one percent level. The same result was true for copper indicating the animals appear to take up the metals in direct proportion to levels in the sediment.

However, not all research has revealed such strong relationships between metal concentrations and a decline in biointegrity. Smith and Kaster (1983) concluded that drainage from a rural highway with a relatively light traffic flow of 7000 – 8000 vehicles per day exerted minimal effect on the macroinvertebrate community. Similarly, Perdikaki and Mason (1999) found no evidence of sediment metal contamination at stations downstream of ten trunk roads in East Anglia and only subtle impairment of the macroinvertebrate communities. The study however, did not isolate surface runoff as the only discharge to the streams, and as the authors themselves confessed, supposedly clean upstream stations may have been polluted by other discharges, masking the effects of road runoff.

As in the Van Hessel *et al*. (1980) and Shutes (1985) the data from the sixty-two Yorkshire sites indicates a decline in macroinvertebrate numbers linked to increasing road densities, traffic numbers and the incidence of braking (Figure 2). The in-stream biological community structures indicate that the small headwater streams in this study have been adversely effected by storm water runoff. Fifty percent of sample stations surveyed were found to have less diverse and contained fewer pollution sensitive taxa than the control site assemblages and only one of the 62 stations was classed as having 'good' biological quality as opposed to the approximately 90 percent predicted by the RIVPACS model.

## 7. ORGANIC CHEMICALS

Natural streamwater conditions are associated with limited organic material and plentiful dissolved oxygen (DO). Limited organic matter restricts microbial populations, and the DO otherwise used in decomposition remains relatively constant. The natural system becomes overloaded when excess anthropogenic inputs enter the receiving water. This may lead to an explosion in the numbers of microbial decomposers and consequent reduction in DO in the water column and sediments. Anoxic conditions arise in instances of severe organic pollution, with both the water column and sediments becoming devoid of oxygen (Andoh, 1994; Haughton and Hunter, 1994).

Research into organic chemicals has focused primarily on compounds that are toxic to plants, animals and humans, and those which are persistent, causing bioaccumulation in organisms and along food chains (Haughton and Hunter, 1994). Organochlorine compounds which include chlorofluorocarbons (CFCs), polychlorinated biphenyls (PCBs), the pesticides aldrin, dieldrin eldrin and dichloro-diphenyl-trichloroethane (DDT), and various dioxins have received much attention. Other substances in solution such as ammonia, nutrients and PAHs may propagate imbalances. Ammonia is toxic to fish above a certain threshold, while nitrates and phosphates can cause eutrophication (Lenat and Crawford, 1994). PAHs although common in the urban environment and increasing because of greater vehicle use have received little attention. In urban storm water discharge PAHs are likely to be the main group of organic contaminants with the greatest potential toxicity.

### 7.1 Polycyclic Aromatic Hydrocarbons (PAHs)

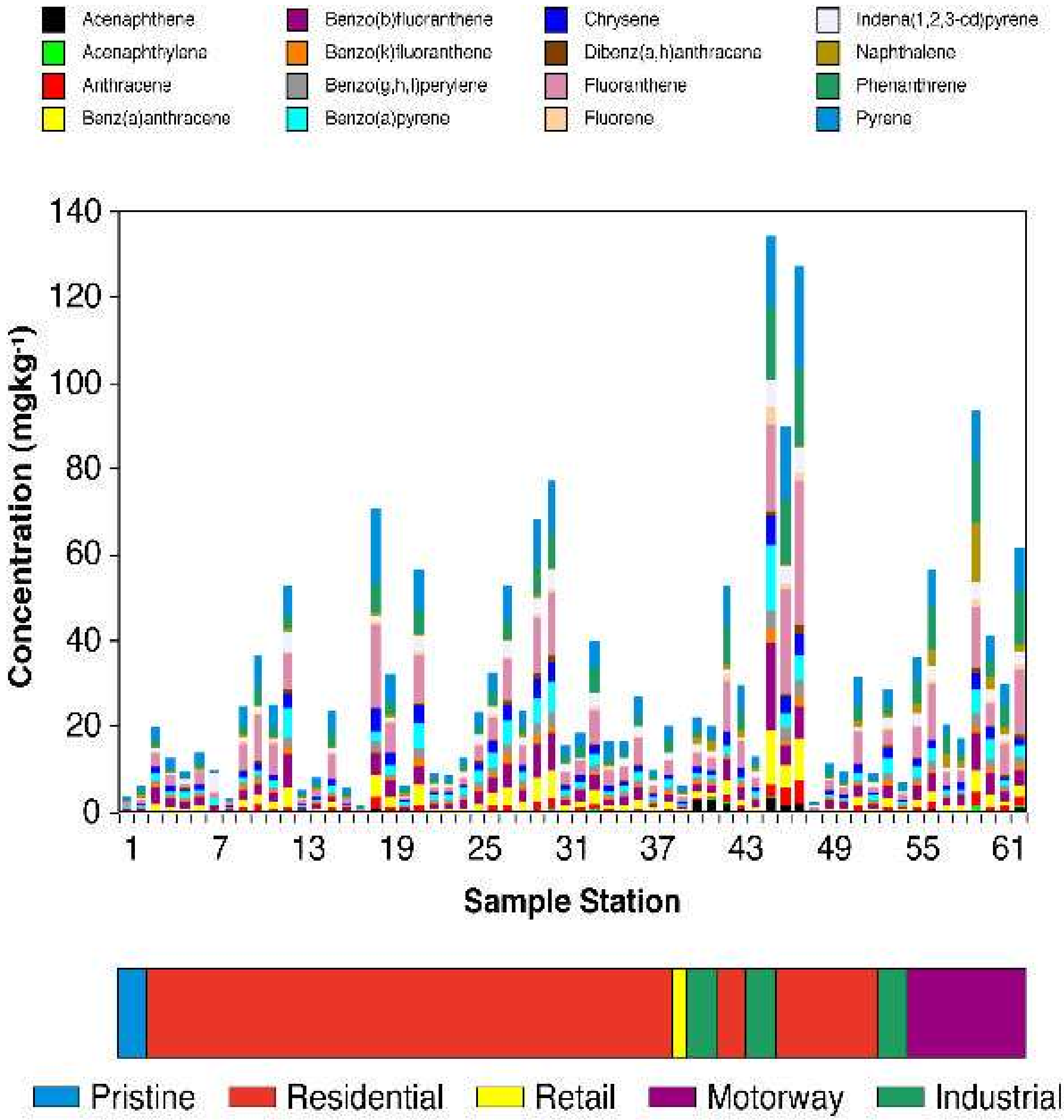
Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrophobic organic compounds with a widespread occurrence in the environment as a consequence of the combustion of fossil fuels and industrial processes. Coring studies have shown that concentrations of PAHs have been increasing over the past 20 – 40 years (van Metre *et al*., 2000) and concurrent with these increases has been a change in the assemblages indicating greater contributions from combustion sources. The increase in concentrations correlates strongly with the increase in vehicle use even in catchments that have not undergone significant land use changes (van Metre *et al*., 2000). Generally a concentration gradient exists from urban and industrial areas to rural areas (Bomboi *et al*., 1999). Given the known carcinogenic properties, particularly of benzo(a)pyrene, benzo(a)anthracene and chrysene in humans and other animals (Christiensen *et al*., 1975; Mastran *et al*., 1994), the fate of PAHs in the environment and identification of sites where they may accumulate to significant concentrations is important. Despite their known toxicities and widespread occurrence, hydrocarbons have received much less attention than heavy metals in water quality studies. There is a noticeable bias in the literature towards research focusing on the marine environment and a paucity of studies concerning the fate and impact of PAHs within freshwater systems.

Early work indicated urban storm water runoff as responsible for a considerable petroleum hydrocarbon load to the environment (Hallhagen, 1973; Wakeham, 1977). As with heavy metals, hydrocarbons preferentially enrich fine particles because of their surface adsorption. MacKenzie and Hunter (1979) identified 86.4 percent of hydrocarbons were associated with particulates, while Hoffman *et al*. (1982) suggested the figure was as high as 93%, highlighting the importance of sediments as the principal sources of PAH exposure to freshwater fauna and flora. Furthermore, evidence exists that PAHs demonstrate the same 'food chain effects' as heavy metals and therefore impact across whole ecotones (Whipple, 1981; Clements *et al*., 1994).

Examining the impacts of storm water runoff from sections of a UK motorway Shutes (1984) and Maltby *et al*. (1995a, 1995b) both found impoverished macroinvertebrate assemblages at the downstream stations. There were fewer pollution sensitive taxa downstream, notably *Gammarus pulex.* Shutes (1984) recorded a decrease in mean monthly numbers from 75 upstream of the M1 discharge to 14.6 downstream and complete eradication at stations 5 – 6 km further downstream. The loss of Diptera from downstream stations meant a reduction in *Erpobdella octoculata*, as Diptera larvae are a known food resource. Impoverishment was attributed to the direct toxic effects of heavy metals and PAHs in the water column and bed sediment as no significant between station differences in either the abundance of epilithic algae or detritus and associated fungi were observed. Furthermore, the major changes observed could not be explained on the basis of changes in substrate particle size or total organic content.

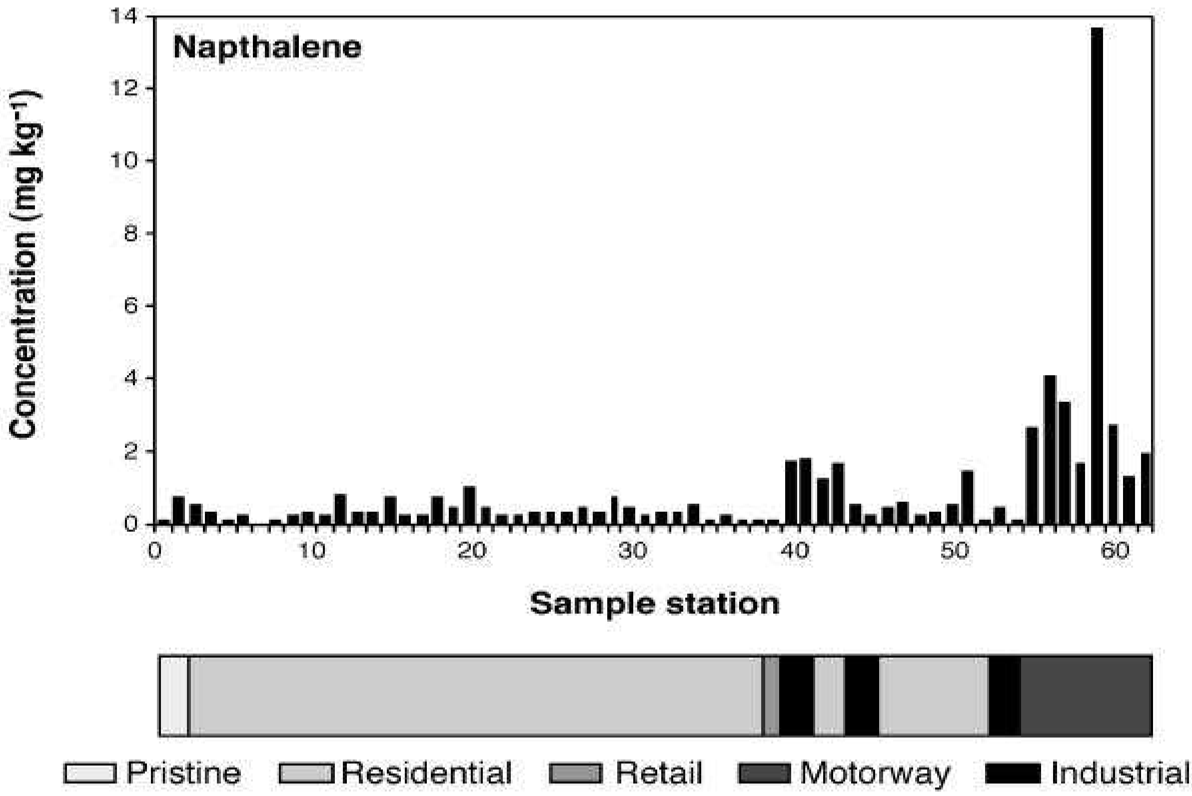
The general distribution pattern of PAHs in sediments in the Yorkshire streams is shown in Figure 7. Figure 8 picks up the distribution of naphthalene as a particular example where its link to the more industrialised and motorway sites is strong. This research also showed detailed variations on the general pattern. Certain residential sub-catchments, for example stations 46 and 47 are capable of contributing higher concentrations of PAHs than motorways as a result of their catchment characteristics. Small affluent residential sub-catchments where the majority of vehicles are stored in off-road garages do not accumulate PAHs to the same degree as housing estates with few garages or where vehicles are predominantly parked on the roadside. Evidence supporting the importance of parked vehicles in producing high PAH levels, particularly fluoranthene, phenanthrene and pyrene comes from stations 45 and 59,

**Figure 7 Total PAH contamination.**



Acenaphthene
Acenaphthylene
Anthracene
Benz(a)anthracene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Benzo(a)pyrene
Chrysene
Dibenz(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene
Concentration (mgkg-1)
0
20
40
60
80
100
120
140
1
7
13
19
25
31
37
43
49
55
61
Sample Station
Pristine
Residential
Retail
Motorway
Industrial

**Figure 8    Sediment concentrations of the PAH  Naphthalene**




where heavily used lay-bys add to high downstream PAH levels.  It is suggested this is due to the increased incidence of fuel and oil leaks onto the surface which are then entrained by storm water runoff.  Vehicle emissions appear to be a less important source of PAHs with the exception of napthalene.  The present research has also found that the concentrations of PAHs are controlled by the physical characteristics of the receiving watercourse.  Large, fast flowing streams with substrates dominated by gravel or cobbles do not provide the opportunity for high PAH levels because of their dilution and dispersion potential.  This may be responsible for masking the true level of PAH contamination from motorways as three of the streams exhibited such characteristics.  Whether station 59 recorded high levels because of the lay-bye or because the stream offered little dispersion potential would require further investigation.

## 8. MODELLING SPECIES – ENVIRONMENT RELATIONS

There are limitations concerning both laboratory and field based investigations. There is a tendency for laboratory bioassays to concentrate on a few sensitive species of uniform age and size, ignoring the heterogeneous responses of a natural population and nutrition, physiological interactions, substrate, stream current, predation and competition factors. Artificial streams provide restricted physical and ecological conditions. Field based research on the other hand, is not capable of determining toxicity thresholds, hence the complementary nature of the techniques. To overcome these deficiencies some researchers have investigated modelling macroinvertebrate assemblages from environmental variables (Brown and May, 2000; Ormerod and Edwards, 1987; Weatherley and Ormerod, 1987). One advantage of this approach is that 'natural' stress parameters are also included (Reinhold-Dudok van Heel and den Besten, 1999). Work that focused on physical variables and catchment characteristics (Armitage *et al*., 1983; Furse *et al*., 1987; Moss *et al*., 1987, Wright *et al*., 1993a, 1993b, 2000), lead to the development of the RIVPACS model currently employed by the EA in the UK and in Australia. RIVPACS predicts BMWP and ASPT scores for pristine watercourses from catchment data including stream width and depth, catchment elevation and particle size.

Contaminants, physical variables and macroinvertebrate species models have been used to study community structures (Gower *et al*., 1994, 1995; Nelson and Roline, 1999; Reinhold-Dudok van

Heel and den Besten, 1999). Reinhold-Dudok van Heel and den Besten (1999) using Redundancy Analysis (RDA) and Canonical Correspondence Analysis (CCA) found that for the sediment types fine sand, sand silt and silt, sediment toxicity explained part of the variation in species composition, but no particular element was identified. Research by Gower *et al.* (1994, 1995) used CCA to examine elevated metal concentrations in the water columns draining mines in the South West of England. They were able to identify copper as the most important determinant in influencing the community structure. A notable finding that agreed with many of the other studies presented here, was the sensitivity of Ephemeroptera to elevated concentrations of metals and the tolerance of Chironimidae. It is evident from the literature that although becoming increasingly common in applied ecology, very few studies exist concerning the relations between macroinvertebrates and environmental contaminants. Moreover, no research was evident investigating bioavailable sediment metal concentrations and PAHs derived from urban storm water runoff – a potentially limiting factor in achieving ecological integrity.

Partial Canonical Correspondence Analysis (PCCA) was used to investigate relationships in the Yorkshire dataset. The heavy metals, 16 PAHs, BMWP data and the environmental variables identical to those recorded for RIVPACs forecasts, were included. Only the bioavailable metals from extract 1 were used. Looking at the metals in isolation showed Zinc, Dissolved oxygen, Electrical Conductivity, Nickel and lead as the most influential factors (Table 9). This contrasts with the studies reviewed here which identified copper as a critical variable. Here it appears eighth. Looking at the results when PAH data is included the most significant controls on macroinvertebrate community composition were found to be zinc, followed by nickel, naphthalene, iron and benzo(b)fluoranthene. Interestingly this mixes metals and PAHs showing the importance of considering their influence in combination (Table 9). The metals and PAHs account for 24% of the variance and the environmental variables account for a further 23%. The important influence of zinc and nickel is clear in both analyses.

**Table 10 First ten rankings from PCCA analyses using weighted total metal concentrations (extract 1); and PAHs and weighted total metal concentrations (extract 1) combined, using unrestricted Monte Carlo significance tests. F values significant at P<0.05**

| Weighted total metal concentrations (extract 1). | | PAHs and weighted total metal concentrations (extract 1) combined. | |
|---|---|---|---|
| ***Variable*** | ***F*** | ***Variable*** | ***F*** |
| Zinc | 3.31 | Zinc | 3.36 |
| Dissolved oxygen | 2.34 | Nickel | 3.14 |
| Electrical Conductivity | 1.76 | Naphthalene | 1.83 |
| Nickel | 1.85 | Iron | 1.46 |
| Lead | 1.94 | Benzo(b)fluoranthene | 1.43 |
| PH | 1.01 | Electrical Conductivity | 1.63 |
| Iron | 1.19 | Fluoranthene | 1.68 |
| Copper | 0.91 | pH | 1.39 |
| Chromium | 0.64 | Indeno(1,2,3-cd)pyrene | 1.34 |
| Cadmium | 0.61 | Dibenz(a,h)anthracene | 1.17 |

Looking in more detail at the ordination diagrams it is clear that sites containing naphthalene tolerant communities are predominantly associated with streams receiving motorway runoff. The sites that have communities tolerant to one or more of the PAHs are associated with streams receiving runoff from mainly industrial land use or from heavily trafficked main 'A' roads. By contrast sites containing communities sensitive to PAH contamination are largely associated with control or lightly trafficked residential land uses. Looking in detail at the macroinvertebrate families the plots show that *Hydrophilidae*, *Physidae*, *Sphaeridae*, *Valvatidae*, *Erpobdellidae*, and *Asellidae* are tolerant indicator species for both metals and PAHs. *Leptoceridae*, *Leptophlebiidae*, *Ephemeridae*, *Hydrometridae* and *Philopotamidae* are indicative of streams with very little contamination by either metals or PAHs.

PCCA reveals that the variables recorded for this study are capable of explaining variations in macroinvertebrate community compositions moderately well, demonstrating the usefulness of the technique in relation to bed sediment quality. Strong relationships are identified from the ordination diagrams and rankings for several variables, particularly zinc. The ordination diagrams successfully differentiate community composition between sites and pick out indicator species for both metals and PAHs independently, and in combination.

## 9. DISCUSSION AND FUTURE DIRECTIONS

Despite evidence that metals and PAH contaminants pose a serious threats to stream ecology this review shows there is relatively little research which explicitly identifies contamination sources within catchments, bioavailable as distinct from total metal concentrations, or the importance of sediments in storing contaminants. Heavy metals and PAHs are of concern because of their increasing release into the environment and their toxicity to aquatic fauna and flora. Trace metals, cobalt, copper, chromium, iron, manganese, nickel, molybdenum, selenium and zinc, are important micronutrients in plant and animal nutrition where they play an essential role in tissue metabolism and growth (Amundsen *et al*., 1997). But severe metal imbalances are toxic and marginal imbalances contribute to deformities and impede health.

Both metals and PAHs preferentially enrich fine particles because of their surface adsorption However, the chemical forms in which they exist determine the bioavailability of these contaminants. The chemical forms of heavy metals are governed by many factors that include their concentration, water hardness, presence and concentration of other metal ions, and organic ligands such as carbonates, and iron and manganese hydroxides. There is a lack of information concerning the factors that influence the bioavailability of PAHs.

Few studies have examinined specific metal toxicities on macroinvertebrates. Laboratory research examining sub-lethal effects demonstrates deleterious changes in growth rates, enzyme activity and reproductive rates of macroinvertebrates subjected to low doses of nickel, copper and zinc. Toxic concentrations have been found to differ for individual species and under different water chemistry. Similarly, there is considerable variation between species concerning lethal toxicity concentrations. Factors such as species life stage, exposure history, and origin in terms of stream order and altitude have been shown to be important in determining metal tolerance. There is agreement in the literature that laboratory assays should be undertaken during a species' early development stage and periods of moult, which are times of exceptional stress and sensitivity. By doing so, guidelines would be set that are capable of effectively protecting macroinvertebrate species. Declines in populations of all major taxon subjected to copper concentrations as low as 5 – 10 $\mu g\ l^{-1}$ have been reported in the literature. Similarly, zinc concentrations as low as 0.3 mg $l^{-1}$ have been shown to reduce the offspring numbers and size of female *Gammarus pulex*.

The aim of the field investigations was to explore relationships between streambed sediment contaminants and macroinvertebrate assemblages in a range of urban streams. The results of this research show the quality of streambed sediments is impaired generally and the importance of looking at both metal and oil contaminants together. The sediments from nearly all the Yorkshire sites have lower BMWP and ASPT scores than the environment-based RIVPACS model forecast (Figure 2). The sites below inputs collecting runoff from housing or roads all show reduced macroinvertebrate numbers. Heavy metals and PAHs are elevated in most sediments compared to the natural, pristine control sites. With few exceptions total concentrations of both contaminant groups in descending order of concentration are motorways > industry > residential > pristine. This order, and detailed variations within the data, suggests that vehicles are a major contributing source of contaminants but by no means the only source.

Previous field studies typically show impoverished macroinvertebrate assemblages downstream of urban runoff discharge points and in streams subjected to mine drainage where there are elevated concentrations of heavy metals. The use of PCCA or CCA has identified copper as a major influence in determining the community composition. Maltby *et al.* (1995b) identified PAHs, copper and zinc as the major toxicants. In this study zinc and nickel are shown to be the more influential metals (Table 9). This may be linked, in part, to the local geology but indicates also the importance of taking samples from a range of sites not just from anticipated problem areas. Clearly this work would benefit from comparative studies at sites with alternative substrates.

The use of ordination techniques identified a metal tolerance continuum identical to that revealed in laboratory toxicity experiments in the order Chironomidae > Trichoptera > Plecoptera > Ephemeroptera. This is encouraging but also points up the lack of parallel research examining PAHs in association with metals. Their omission may mean the metal results are less informative about the causes of impoverished macroinvertebrate assemblages. The PCCA analyses have explained 47% of the variation in macroinvertebrate assemblages in the Yorkshire dataset and the importance of looking at oils and metals together

Ecological water quality has been qualitatively linked to road traffic flows, observations of oil leaks, braking and urbanisation factors for sites in Yorkshire. There is need for research on downstream persistence of urban runoff pollutants and into the long-term impacts of metal and oil contamination in streams that have a historic legacy of receiving CSOs, point source pollution. Such information concerning the severity and spatial extent of any downstream impairment is important for prioritising sub-catchments for control measures. These data should be integrated with a GIS holding traffic flow, car ownership, parking and more detailed land use information to more explicitly account for catchment and anthropogenic influences. Given that urban runoff is influenced by spatial factors relating to stream and catchment characteristics a GIS is the most appropriate tool for storing and analysing such data. A GIS based forecasting tool could further our understanding of the relationships between variables such as catchment size, catchment topography, vehicle flows, population densities, surrounding habitat quality and catchment hydrology with streambed sediment contamination and macroinvertebrate community compositions.

There is a tension between the time and expense involved in detailed catchment studies, which can tease out the local relationships and the need to forecast at the larger scale. In the long term these results could contribute towards the development of a RIVPACS type model for contaminated streams, but local studies are a fundamental step towards the more global model. At present there is a lack of local data that quantitatively links individual contaminants with specific catchment characteristics which impedes current forecasting.

## REFERENCES


Amundsen, P., Staldvik, F. J., Lukin, A. A., Kashulin, N. A., Popova, O. A. and Reshetnikov, Y. S. 1997 Heavy metal contamination in freshwater fish from the border region between Norway and Russia. *Science of the Total Environment*, 201, 371-378.

Amyot, M., Pinelalloul, B. and Campbell, P. G. C. 1994 Abiotic and seasonal factors influencing trace-metal levels (Cd, Cu, Ni, Pb, and Zn) in the fresh-water amphipod *Cammarusfasiatus* in 2 fluvial lakes of the St-Lawrence-River. *Canadian Journal of Fisheries and Aquatic Sciences*, 51, 9, 2003-2016.

Andoh, R. Y. G. 1994 Urban runoff: nature, characteristics and control. *Journal of the Institution of Water and Environmental Management*, 8, 371-378.

Ankley, G. T., Lodge, K., Call, D. J., Baker, M. D., Brooke, L. T., Cooke, P. M., Kreis, R. G., Carlson, A. R., Johnson, R. D., Niemi, G. J., Hoke, R. A., West, C. W., Giesy, J. O., Jones, P. D. and Fuying, Z. C. 1992 Integrated assessment of contaminated sediments in the Lower Fox River and Green Bay, Wisconsin. *Ecotoxicol*ogy and *Environmental Safety*, 23, 46-63.

Armitage, P. D., Moss, D., Wright, J. F. and Furse, M. T. 1983 The performance of a new biological water quality score system based on macroinvertebrates over a wide range of unpolluted running-water sites. *Water Resources*, 17, 333-347.

Bannerman, R. T., Owens, D. W., Dodds, R. B. and Hornewer, N. J. 1993 Pollutants in Wisconsin stormwater. *Water Science and Technology,* 28, 241-259.

Beyer, W. N., Day, D., Melancon, M. J. and Sileo, L. 2000 Toxicity of Anacostia River, Washington DC, USA, sediment fed to Mute Swans (*Cygnus olor*). *Environment Toxicology and Chemistry*, 19, 3, 731-735.

Biney, C., Amuzu, A. T., Calamari, D., Kaba, N., Mbome, I. L., Naeve, H., Ochumba, P. B. O., Osibanjo, O., Radegonde, V. and Saah, M. A. H. 1994 Review of heavy metals in the African aquatic environment. *Ecotoxicology and Environmental Safety,* 28, 2, 134-159.

Bomboi, M. T., Mendez, J., Grimals, J., Prada, D. and Cerda, V. 1999 Polycyclic aromatic hydrocarbons in ambient air: a view of some obtained results in Spain in the last years. *Fresenius Environmental Bulletin*, 8, 9-10, 595-601.

Boyle, R. W. and Robinson, H. A. 1988 Nickel in the natural environment..In Sigel, H. editor, *Metal Ions in Biological Systems*, New York: Marcel Dekker Inc, 1-29.

Brown, L. R. and May, J. T. 2000 Macroinvertebrate assemblages on woody debris and their relations with environmental variables in the Lower Sacramento and San Joaquin river drainages, California. *Environmental Monitoring and Assessment*, 64, 211-329.

Casper, A. F. 1994 Population and community effects of sediment contamination from residential urban runoff on benthic macroinvertebrate biomass and abundance. *Bulletin of Environmental Contamination and Toxicology*, 53, 796-799.

Catallo, W. J. and Gambrell, R. P. 1987 The effects of high levels of PAH on sediment physiochemical properties and benthic organisms in a polluted stream. *Chemosphere*, 16, 1053-1063.

Chandler, R. D. 1994 Estimating annual urban nonpoint pollution loads. *Journal of Management in Engineering*, 10, 6, 50-59.

Characklis, G. W. and Wiesner, M. R. 1997 Particles, metals and water quality in runoff from large urban watershed. *Journal of Environmental Engineering*, 123, 8, 753-759.

Chaudhry, H. S. and Kedarnath, P. 1985 Nickel-induced hyperglycemia in the freshwater fish, *Colisa fasciatus..Water, Air and Soil Pollution*, 24, 173-176.

Christiensen, H. E., Lugin Byhl, T. T. and Carroll, B. S. 1975 *Registry of Toxic Effects of Chemical Substances,* Rockville, Maryland: US Dept. H. E. W.

Ciborowski, J. J. H. and Corkum, L. D. 1988 Organic contaminants in adult aquatic insects of the St Clair and Detroit Rivers, Ontario, Canada. *Journal of the Great Lakes Research*, 14, 148-156.

Clements, W. H. 1991a Characterization of stream benthic communities using substrate-filled trays colonization, variability, and sampling selectivity. *Journal of Freshwater Ecology*, 6, 2, 209-221.

Clements, W. H. 1991b Community responses of stream organisms to heavy metals: a review of observational and experimental approaches. In Newman, M. C. and McIntosh, A. W. editors, *Metal Ecotoxicology: Concept and Applications*, Chelsea, Michigan: Lewis Publishers, 363-391.

Clements, W. H. and Kiffney, P. M. 1995 The influence of elevation on benthic community responses to heavy-metals in rocky-mountain streams. *Canadian Journal of Fisheries and Aquatic Sciences*, 52, 9, 1966-1977.

Clements, W. H., Oris, J. T. and Wissing, T. E. 1994 Accumulation and food-chain transfer of fluoranthene and benzo[a]pyrene in chironomus-riparius and lepomis-macrochirus. *Archives of Environmental Contamination and Toxicology*, 26, 3, 261-266.

Clements, W. H. and Rees, D. E. 1997 Effects of metals on prey abundance, feeding habitats and metal uptake of brown trout in the Arkansas River, Colorado. *Transactions of the American Fisheries Society*, 126, 5, 774-785.

Cook, S. E. K. 1976 Quest for an index of community structure sensitive to water pollution. *Environmental Pollution*, 11, 269-287.

Courtney, L. A. and Clements, W. H. 2000 Sensitivity to acidic pH in benthic invertebrate assemblages with different histories of exposure to metals. *Journal of the North American Benthological Society*, 19, 1, 112-127.

Dermott, R. M. and Lum, K. R. 1986 Metal concentrations in the annual shell layers of the bivalve *Elliptio complanata. Environmental Pollution (Series B) EPSPDH*, 12, 131-143.

EA (Environment Agency) 1997 *Assessing Water Quality – General Quality Assessment (GQA) Scheme for Biology.* Environment Agency fact sheet, Bristol: Environment Agency.

EBI (Environmental Bureau of Investigation) 1998 *Contaminants: Zinc*, [online] available from <http://www.nestcity.com/ebi/contaminants//zinc.htm> [Accessed on 13 July 1998]

EIFAC (European Inland Fisheries Advisory Commission) 1984 *Report on Nickel and Freshwater Fish.* EIFAC T/45, Rome: FAO.

Ellis, J. B. and Hvitved-Jacobsen, T. 1996 Urban drainage impacts on receiving waters. *Journal of Hydraulic Research*, 34, 6, 771-783.

Estèbe, A., Boudries, H., Mouchel, J. M. and Thevenot, D. R. 1997 Urban runoff impacts on particulate metal and hydrocarbon concentrations in the River Seine, suspended solid and sediment transport. *Water Science and Technology*, 36, 8-9, 185-195.

Faulkner, H., Edmons-Brown, V. and Green, A. 2000 Problems of quality in diffusely polluted urban streams – the case of Pymme's Brook, North London. *Environmental Pollution*, 109, 91-107.

Furse, M. T., Moss, D., Wright, J. F. and Armitage, P. D. 1987 Fresh-water site assessment using multi-variate techniques. In Luff, M. L. editor, *The Use of Invertebrates in Site Assessment for Conservation.* Agricultural Environment Research Group, University of Newcastle-upon-Tyne.

Giesy, J. P., Graney, J. L., Newsted, C. J., Rosiu, A., Benda, R. G., Kries, Jr. and Horvath, F. J. 1988 Comparison of three sediment bioassays using Detroit River sediments.*Environment Toxicology and Chemistry*, 7, 483-498.

Goodyear, K. L. and McNeill, S. 1999 Bioaccumulation of heavy metals by aquatic macro-invertebrates of different feeding guilds: a review. Sc*ience of the Total Environment*, 229, 1-19.

Gower, A. M., Myers, G., Kent, M. and Foulkes, M. E. 1994 Relationships between macroinvertebrate communities and environmental variables in metal-contaminated streams in south-west England. *Freshwater Biology*, 32, 199-21.

Gower, A. M., Myers, G., Kent, M. and Foulkes, M. E. 1995 The use of marcroinvertebrate assemblages in the assessment of metal – contaminated streams. In Harper, D. M. and Ferguson, A. J. D. editors, *The Ecological Basis for River Management*, Chichester: John Wiley.

Griffiths, R. W. 1991 Environmental quality assessment of the St. Clair River as reflected by the distribution of benthic macroinvertebrates in 1985. *Hydrobiologia*, 219, 143-164.

Hallhagen, A. 1973 *Survey of Present Knowledge and Discussion of Input of Petroleum to the Marine Environment in Sweden.* Oral Paper presented at workshop on Inputs, Fates and Effects of Petroleum in the Marine Environment, National Academy of Sciences.

Harrahy, E A. and Clements, W. H. 1997 Toxicity and bioaccumulation of a mixture of heavy metals in *Chironomus tentans* (Diptera: Chironomidae: in synthetic sediment. *Environmental Toxicology and Chemistry*, 16, 2, 317-327.

Haslam, S. M. 1990 *River Pollution: An Ecological Perspective.* London: Belhaven Press.

Haughton, G. and Hunter, C. 1994 *Sustainable Cities.* 2nd Edition., London: Jessica Kingsley.

Hickney, C. W. and Clements, W. H. 1998 Effects of heavy metals on benthic macroinvertebrate communities in New Zealand streams. *Environmental Toxicology and Chemistry*, 17, 1, 2338-2346.

Hoffman, E. J., Latimar, J. S., Mills, G. L. and Quinn, J. G. 1982 Petroleum hydrocarbons in urban runoff from a commercial land use area. *Journal of Water Pollution Control Federation*, 54, 1517-1525.

House, M. A., Ellis, J. B., Herricks, E. E., Hvitved-Jacobsen, T., Seager, J., Lijklema, L., Aalderink, H. and Clifforde, I. T. 1993 Urban drainage – impacts on receiving water quality. *Water Science and Techonology*, 27, 12, 117-158.

Jenkins, D. W. 1980 Nickel accumulation in aquatic biota. In Nriagu, J. O. editor, *Nickel in the Environment*, New York: John Wiley, 283-338.

Karr, J. R. and Chu, E. W. 2000 Sustaining living rivers. *Hydrobiologia*, 422, 1-14.

Katalin, V. B. 1988 Heavy metal pollution from a point source demonstrated by mussel (*Unio pictorum*) at Lake Balaton, Hungry. *Bulletin of Environmental Contamination and Toxicology*, 41, 247-263.

Kemp, S. J. and Spotila, J. R. 1997 Effects of urbanisation on brown trout *Salmo trutta*, other fishes and macroinvertebrates in Valley Creek, Valley Forge, Pennsylvania. *American Midland Naturalist*, 138, 55-68.

Kiffney, P. M. and Clements, W. H. 1994a Effects of heavy metals on a macroinvertebrate assemblage from a rocky mountain stream in experimental microcosms. *Journal of the Northern American Benthological Society*, 13, 4, 511-523.

Kiffney, P. M. and Clements, W. H. 1994b Structural responses of benthic macroinvertebrate communities from different stream orders to zinc. *Environmental Toxicology and Chemistry*, 13, 3, 389-395.

Kiffney, P. M. and Clements, W. H. 1996a Size-dependent response of macroinvertebrates to metals in experimental streams, *Environmental Toxicology and Chemistry.* 15, 8, 1352-1356.

Kiffney, P. M. and Clements, W. H. 1996b Effects of metals on stream macroinvertebrate assemblages from different altitudes. *Ecological Applications*, 6, 2, 472-481.

Lazaro, T. R. 1990 *Urban Hydrology, A multidisciplinary perspective.* Lancaster, Pennsylvania: Technomic Publishing.

Lee, J. H. and Bang, K. W. 2000 Characterization of urban stormwater runoff. *Water Research*, 34, 6, 1773-1780.

Leland, H. V., Fend, S. V., Dudley, T. L. and Carter, J. L. 1989 Effects of copper on species composition of benthic insects in a Sierra Nevada, California. *Stream and Freshwater Biology*, 21, 163-179.

Lenat, D. R. and Crawford, J. K. 1994 Effects of land use on water quality and aquatic biota of three North Carolina piedmont streams. *Hydrobiologia*, 294, 185-199.

MacKenzie, M. J. and Hunter, J. V. 1979 Sources and fates of aromatic compounds in urban stormwater runoff. *Environmental Science Technology,* 13, 179-183.

Makepeace, D. K., Smith, D. W. and Stanley, S. J. 1995 Urban stormwater quality- summary of contaminant data. *Environmental Science Technology*, 25, 2, 93-139.

Malmqvist, P. A. 1983 *Urban Stormwater Pollutant Sources*, Chalmers University of Technology, Gothenburg.

Maltby, L., Boxall, A. B. A., Forrow, D. M., Calow, P. and Betton, C. I. 1995a The effects of motorway runoff on freshwater ecosystems: 2. Identifying major toxicants. *Environmental Toxicology and Chemistry*, 14, 6, 1093-1101.

Maltby, L., Forrow, D. M., Boxall, A. B. A., Calow, P. and Betton, C. I. 1995b The effects of motorway runoff on freshwater ecosystems: 1. Field study. *Environmental Toxicology and Chemistry*, 14, 6, 1079-1092.

Maltby, L. and Naylor, C. 1990 Preliminary observations on the ecological relevance of the *Gammarus* 'scope for growth' assay: effect of zinc on reproduction. *Functional Ecology*, 4, 393-397.

Mance, G., Brown, V. M. and Yates, J. 1984 *Proposed Environmental Quality Standards for List II Substances in Water – Copper.* Water Research Centre Technical Report, Water Resource Centre, Buckinghamshire, UK.

Marsalek, J. 1990 Evaluation of pollutant loads from urban nonpoint sources. *Water Science and Technology*, 22, 10-11, 23-30.

Marsalek, J., Rochfort, Q., Brownlee, B., Mayer, T. and Servos, M. 1999 An explanatory study of urban runoff toxicity. *Water Science and Technology*, 39, 12, 33-39.

Mastran, T. A., Dietrich, A. A., Gallagher, D. L. and Grizzard, T. J. 1994 Distribution of polyaromatic hydrocarbons in the water column and sediments of a drinking water reservoir with respect to boating activity. *Water Research*, 28, 11, 2353-2366.

McCall, P. L. and Soster, F. M. 1990 Benthos response to disturbance in Western Lake Erie: regional faunal surveys. *Canadian Journal of Fisheries and Aquatic Sciences*, 47, 1996-2009.

McCormick, P. V. and Cairns, J. 1994 Algae as indicators of environmental change. *Journal of Applied Phycology*, 6, 509-526.

Metcalfe, J. L. 1989 Biological water quality assessment of running waters based on macroinvertebrate communities: history and present status in Europe. *Environmental Pollution*, 60, 101-139.

Milbrink, G. 1983 An improved environmental index based on the relative abundance of Oligochaete species. *Hydrobiologia*, 102, 89-97.

Moog, O. and Chovanec, A. 2000 Assessing the ecological integrity of rivers: walking the line among ecological, political and administrative interests. *Hydrobiologia*, 422, 99-109.

Moore, W. M. and Ramamoorthy, S. 1984 Heavy Metals in Natural Waters: Applied Monitoring and Impact Assessment. New York: Springer-Verlag.

Moss, D., Furse, M. T., Wright, J. F. and Armitage, P. D. 1987 The prediction of the macro-invertebrate fauna of unpolluted running-water sited in Great Britain using environmental data. *Freshwater Biology*, 17, 41-52.

Mulliss, R. M., Ellis, J. B., Revitt, D. M. and Shutes, R. B. E. 1994 An evaluation of the toxic influences on asellus-aquaticus (L) in an urban stream environment. *Water Science and Technology*, 29, 119-207.

Mulliss, R. M., Revitt, D. M. and Shutes, R. B. E. 1996a A statistical approach for the assessment of the toxic influences on *Grammarus pulex* (Amphipoda) and *Asellus aquaticus* (Isopoda) exposed to urban aquatic discharges. *Water Research*, 30, 5, 1237-1243.

Mulliss, R. M., Revitt, D. M. and Shutes, R. B. E. 1996b The determination of the toxic influences to *Gammarus pulex* (Amphipoda) caged in urban receiving waters. *Ecotoxicology*, 5, 209-215.

National Safety Council 1997 *Environment Writer Zinc (Zn) Chemical Backgrounder*. [online] available from <http://www.nsc.org/ehc/EW/CHEMS/zinc.htm> [Accessed on 13 July 1998]

Nelson, S. M. and Roline, R. A. 1996 Recovery of a stream macroinvertebrate community from mine drainage disturbance. *Hydrobiologia*, 339, 73-84.

Nelson, S. M. and Roline, R. A. 1999 Relationships between metals and hyporpheic invertebrate community structure in a river recovering from metals contamination. *Hydrobiologia*, 397, 211-226.

Novotny, V. 1995 Diffuse sources of pollution by toxic metals and impact on receiving waters. In Salomons, W., Fostner, V. and Mader, P. editors, *Heavy Metals, problems and solutions*, New York: Springer, 33-52.

Ogbeibu, A. E. and Victor, R. 1989 The effects of road and bridge construction on the bank-root macrobenthic invertebrates of a southern Nigerian stream. *Environmental Pollution*, 56, 85-100.

Ormerod, S. J. and Edwards, R. W. 1987 The ordination and classification of macroinvertebrate assemblages in the catchment of the River Wye in relation to environmental factors. *Freshwater Biology*, 17, 533-546.

Perdikaki, K. and Mason, C. F. 1999 Impact of road runoff on receiving streams in Eastern England. *Water Research*, 33, 7, 1627-1633.

Phillips, D. J. H. and Rainbow, P. S. 1993 *Biomonitoring of Trace Aquatic Contaminants.* Elsevier, London.

Pitt, R. and Barron, P. 1989 Assessment of urban and industrial stormwater runoff toxicity and the evaluation/development of treatment for runoff toxicity abatement phase. A report to the US EPA, Edison, New York.

Pitt, R., Field, R., Lalor, M. and Brown, M. 1995 Urban stormwater toxic pollutants: assessment, sources and treatability. *Water Environment Research*, 67, 3, 260-275.

Plante, C. and Downing, J. A. 1989 Production of freshwater invertebrate populations in lakes, *Canadian Journal of Fisheries and Aquatic Sciences.* 46, 1489-1498.

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

Quek, U. and Forster, J. 1993 Trace metals in roof runoff. *Water, Air and Soil Pollution*, 68, 373-389.

Radhakrishnaiah, K., Suresh, A. and Sivaramakrishna, B. 1993 Effect of sub lethal concentration of mercury and zinc on the energetics of a freshwater Fish *Cyprinus carpio* (Linnaeus). *Acta Biologica Hungarica*, 44, 375-385.

Reinhold-Dudok van Heel, H. C. and den Besten, P. J. 1999 The relation between macroinvertebrate assemblages in the Rhine-Meuse Delta (the Netherlands) and sediment quality. *Aquatic Ecosystem Health and Management*, 2, 19-38.

Rochfort, Q., Grapentine, L., Marsalek, J., Brownlee, B., Reynoldson, T., Thompson, S., Milani, D. and Logan, C. 2000 Using benthic assessment techniques to determine combined sewer overflow and stormwater impacts in the aquatic ecosystem. *Water Quality Research Journal of Canada*, 35, 3, 365-397.

Salomons, W., de Rooji, N. M., Kerdijik, H. and Bril, J. 1987 Sediment as a source of contaminants? *Hydrobiologia*, 149, 13-30.

Sansalone, J. J. and Buchberger, S. G. 1997 Partitioning and first flush of metals in urban roadway storm water. *Journal of Environmental Engineering*, 123, 2, 134-143.

Shutes, R. B. E. 1984 The influence of surface runoff on the macroinvertebrate fauna of an urban stream. *Science of the Total Environment*, 33, 271-282.

Shutes, R. B. E. 1985 A comparison of the benthic macroinvertebrate fauna of two north London streams. *Environmental Technology Letters*, 6, 395-404.

Sibly, R. M. and Calow, P. 1985 Classification of habitats by selection pressures: a synthesis of life-cycle and r/K theory. In Sibly, R. M. and Smith, R. H. editors, *Behavioural Ecology*, Oxford: Blackwell, 75-90.

Smith, M. E. and Kaster, J. L. 1983 Effects of rural highway runoff on stream benthic macroinvertebrates. *Environmental Pollution*, A32, 157-170.

Sreedevi, P., Sivaramakrishna, B., Suresh, A. and Radhakrishnaiah, K. 1992a Effect of nickel on some aspects of protein metabolism in the gill and kidney of the freshwater fish, *Cyprinus carpio L. Environmental Pollution*, 77, 59-63.

Stokes, P. 1988 Nickel in aquatic systems, In Sigel, H. editor, *Metal Ions in Biological System.* New York: Marcel Dekker Inc., 31-46.

Taylor, B. R. and Roff, J. C. 1986 Long-term effects of highway construction on the ecology of a southern Ontario stream. *Environmental Pollution*, A40, 317-344.

van Hessel, J. H., Ney, J. J. and Garling, D. L. Jr. 1980 Heavy metals in a stream ecosystem at sites near highways. *Transactions of the American Fisheries Society*, 109, 636-643.

van Metre, P. C., Mahler, B. J. and Furlong, E. T. 2000 Urban sprawl leaves its PAH signature. *Environmental Science and Technology*, 34, 19, 4064-4070.

Wakeham, S. G., 1977 A characterization of the sources of petroleum hydrocarbons in Lake Washington. *Journal of Water Pollution Control Federation*, 49, 1680-1689.

Walley, W. J. and Fontama, V. N. 1998 New approaches to the biological classification of river quality based upon artificial intelligence. In Furse, M. T. and Wright, J. F. editors, *RIVPACS International Workshop*, Oxford, 34-39.

Weatherley, N. S. and Ormerod, S. J. 1987 The impact of acidification on macroinvertebrate assemblages in Welsh streams: towards an empirical model. *Environmental Pollution*, 46, 223-240.

Whipple, J. A. 1981 An ecological perspective of the effects of monocyclic aromatic hydrocarbon on fishes. In Calabazas, F. J., Thurberg, F. P. and Vernberg, W. B. editors, *Biological Monitoring of Marine Pollutants*, New York: Academic Press, 89-105.

Whiting, E. R. and Clifford, H. F. 1983 Invertebrate and urban runoff in a small northern stream, Edmonton, Alberta, Canada. *Hydrobiologia*, 102, 73-80.

Wilber, W. G. and Hunter, J. V. 1979 The impact of urbanization on the distribution of heavy metals in bottom sediments of the Saddle River. *Water Resources Bulletin*, 15, 3, 790-800.

Wright, J. F. 2000 An introduction to RIVPACS. In Wright, J.F., Sutcliffe, D.W. and Furse, M.T. *Assessing the biological quality of fresh waters: RIVPACS and other techniques*. Cumbria: Freshwater Biological Association 1-24.

Wright, J. F., Furse, M. T. and Armitage, P. D. 1993a RIVPACS – a technique for evaluating the biological quality of rivers in the UK. *European Water Pollution Control*, 3, 4, 15-25.

Wright, J. F., Furse, M. T., Armitage, P. D. and Moss, D. 1993b New procedures for identifying running – water sites subject to environmental stress and for evaluating sites for conservation, based on the macroinvertebrate faunna. *Archiv Fur Hydrobiologie,* AHYBA4, 127, 3, 319-326.