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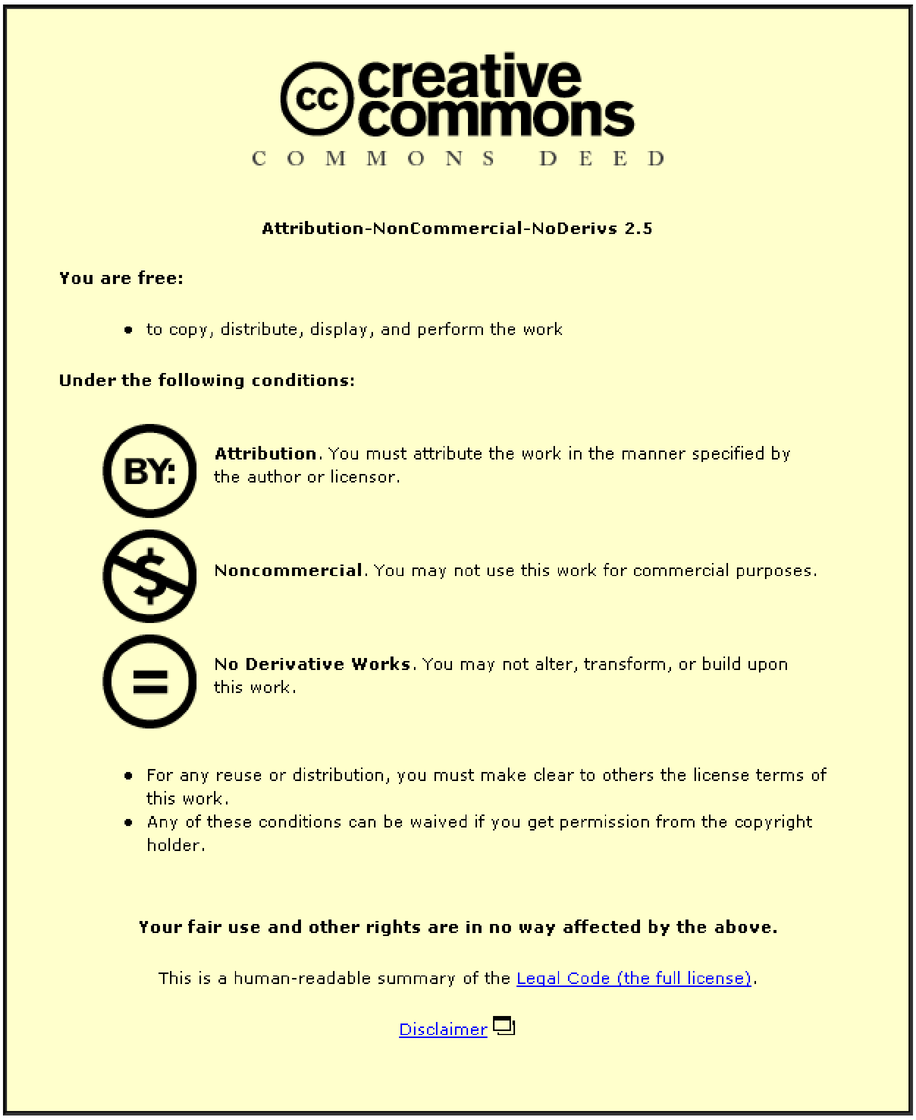

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HIGHWAY DRAINAGE AS A COMPONENT OF METAL INPUT INTO THE CATCHMENT

by Yulia S. Zakharova

CIVIL AND BUILDING ENGINEERING DEPARTMENT
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DOCTORAL THESIS

2010

ABSTRACT

Highway runoff, as a nonpoint source, may exert significant pollutant load on the catchment. Finding ways to mitigate nonpoint sources of pollutants is a matter of great concern for improving water quality. It was cited by the Environment Agency in 2005 that "… more than 80% of English rivers were at risk of failing to achieve Water Framework Directive (WFD) objectives through diffuse pollution…" (Faram, 2007; p.14).

The presence and behaviour of metals were analysed and compared through seasonal sampling from one of the most trafficked roads in the Midlands, M1. These were compared with other sources: local streams and sewage works. The concentration of metals in stormwater from the M1, three neighbouring rural brooks and three local sewage works, all in the same catchment, were sampled. Three metals (Fe, Cu and Zn) were used as an indicator because of their predominance and potential harmful effect on biodiversity. The data was analysed to establish any links between the total and dissolved metals and standard water quality parameters. The thesis also examines the performance of a standard highway treatment system of interceptor and lagoon for removing metals.

The results indicate that evaporation and de-icer salts had the strongest effect on metal concentrations and their solubility in the runoff from the M1. As additional factors, rainfall intensity and antecedent dry weather period (ADWP) had the most important influence on metal concentrations. Fe was always at the highest concentrations for all weather conditions (total and dissolved) and all sampling locations. The results also showed that Fe was affiliated with the particulate matter; however, it was also suggested that it was solubilised by anaerobic conditions. Zn_{tot} during wet weather exceeded the environmental quality standards (EQS) both on the M1 and in Woodbrook. The sewage work effluent did not exceed the EQS at any time of sampling. It was also found that Zn solubility was increased by the presence of de-icer salts which released it from the sediment by a process of ion-exchange, as suggested by the literature. Cu concentrations had the most erratic values and varied widely but were in the lowest concentrations compared to other metals. During wet weather Cu_{dis} from the M1 runoff exceeded the EQS. It was also concluded that the analytical and sample preservation methods chosen could have an effect on the concentrations of copper.

Filtration with recycled glass and pea-gravel was able to remove particles down to 5 μm, but at the typical flow rate (5 m/hr), and solids loading the filters would need regular washing. The adsorption studies showed that metals are more effectively removed by alkaline conditions than acid conditions which release metals into the environment.

Key words: heavy metals; highway runoff; residential runoff; sewage works discharges; SUDS; filtration

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CERTIFICATE OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this thesis, that the original work is my own except as specified in acknowledgments or in footnotes, and that neither the thesis nor the original work contained therein has been submitted to this or any other institution for a degree.

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28/09/2010 (Date)

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List of Symbols & Abbreviations

As	Arsenic
$CaCO_3$	Carbonate of calcium
Cd	Cadmium
Cr	Chromium
Cu	Copper
Fe	Iron
Hg	Mercury
HCl	Hydrochloric acid
HNO_3	Nitric acid
MB	Methylene blue
Na	Sodium
Ni	Nickel
NO_3	Nitrates
P	Phosphorus
PO_4	Phosphates
Pb	Lead
Zn	Zinc

ADT	Annual daily traffic
ADWP	Antecedent dry weather period
EMC	Event mean concentration
HRT	Hydraulic retention time
PEMC	Partial event mean concentration
PSD	Particle size distribution
SUDS	Sustainable urban drainage system

COD	Chemical oxygen demand
DOC	Dissolved organic carbon

NOM	Natural organic matter
EC	Electro-conductivity, µs/cm
TSS	Total suspended solids
TDS	Total dissolved solids
TVS	Total volatile solids
TOC	Total organic carbon
RO	Reverse osmosis
SSA	Specific surface area

AAS	Atomic absorption spectrometry
DPASV	Differential pulse anodic stripping voltammetry
GFAAS	Graphite furnace atomic absorption spectrometry
ICP	Inductively coupled plasma analyser
ICP-MS	Inductively coupled plasma mass spectrometry analyser
ICP-AES	Inductively coupled plasma atomic emission spectrometry analyser
ICP-OES	Inductively coupled plasma optical emission spectrometry analyser
ICP-SFMS	Inductively coupled plasma sector field mass spectrometry analyser

CWC	Clean Washington Centre
USEPA	U.S. Environmental Agency
VDOT	Virginia Department of Transportation
WHO	World Health Organisation

C_i	Individual measurement of the concentration, mg/l
C_{tot}	Total metal concentration, mg/l
C_{part}	Particulate metal concentration, mg/l
C_{dis}	Dissolved metal concentration, mg/l
f_{dis}	Dissolved metal fraction
K_p	Partition coefficient
x	Metal concentration of the particulate phase expressed on a dry weight solid basis, µg/mg
Q	Peak flow, l/s
Q_i	Flow rate at the time concentration C_i was measured, l/s; m^3/s
Δt_i	Time interval associated with C_i, min
d.w.	Dry weight
nm	Nanometres
µm	Microns
ppm	Parts per million
NTU	Nephelometric turbidity units
µS/cm; uS/cm	Micro Siemens per centimetre
$\overline{X}$	Mean value
S	Standard deviation
C_v	Coefficient of variation

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CHAPTER 1

INTRODUCTION

Roads and highways may represent a small part of the impermeable urban catchment area (from 10 to 20%), but road runoff could, according to some, contribute between 35 and 75% of total metal and 50% of the TSS loads to receiving waters (USGS, 2000). The problems associated with urban stormwater treatment and disposal have acquired increased importance due to recent flooding problems and the introduction of the Water Framework Directive (UK Government, 2007). Globally, vehicular traffic is growing very fast and thus it is assumed and suggested that pollutants from vehicular traffic could be more of a problem in future than other urban pollutants because they are diffuse, increasing quantities are being produced and because of their potential persistence and toxicity (Crabtree et al., 2008; Gnecco et al., 2005). This thesis investigates this issue.

Rainfall in England varies widely and the Lake District is the wettest part of the country, with average annual totals exceeding 2000 mm. Rainfall characteristics, such as rainfall intensity and duration, can vary widely from year to year and in November 2009, part of the sampling period, this was demonstrated by the 314.4mm of rain which fell in Cockermouth, Cumbria on 20/11/09 over 24 hours, a once-in-500 years event (Simons, 2009). However, all of East Anglia, much of the Midlands, eastern and north-eastern England and parts of the south-east receive less than 700 mm a year. The East Midlands, the sampling area, experienced high rainfall throughout November 2009 with 145.8mm of rain falling over the whole month (metoffice.gov.uk, 2009; see also Appendix 1 for details. Thus rainfall trends are changing and the impact this could have on highway runoff needs research.

The usual indicator metals are Cu and Zn, since Cu is released from brake linings and Zn from tyres. Moreover, extreme weather events or the accumulation of pollutants in sediments or biota could cause chronic environmental problems. Even in low concentrations, the release of these metals could, given the high traffic volumes, be an important source of metals which impact on aquatic biodiversity. There have therefore been a number of studies which have attempted quantitative analysis of this mass of pollutant and its impact on the chemical and ecological status of receiving waters. Typical factors included in these previous models were rainfall intensity and duration, traffic flow, climate, antecedent dry weather period (ADWP) and first flush characteristics (Novotny and Witte, 1997; Lee et al., 2004; Davis and McCuen, 2005; Herngren et al., 2005; Kim et al., 2005; Crabtree et al., 2006; Li et al., 2006). However, little information about correlations among these factors was found and universally accepted definitions of them may not even exist.

There is little information about Fe, due to its low toxicity, even though it is suggested that Fe will occur in high concentrations in urban runoff as a result of both general usage and vehicle wear (Davis and McCuen, 2005). Iron, despite its low toxicity, is a good model of insoluble materials and of interactions with other metals. Its poor solubility also means that there is the potential for interaction with other metals and solids.

The polluting behaviour of metals will depend on their solubility and therefore their ability to affiliate with, and the amounts of, particulate matter in the runoff. It is suggested that this binding will be affected by factors such as pH, ionic strength, temperature, hardness (base cations), anions, oxidation-reduction potential (redox), and the presence of other elements (USGS, 2000).

Few researchers have attempted to explore these fundamental interactions which will affect the release of metals into the water environment. Much of the literature reviewed fails to indicate whether metals are measured as total or soluble metal, although often this can be assumed to be soluble because of the analytical methods used. This could be a major flaw in the models because of the equilibrium between solid and liquid phases. There is also little previous work attempting to establish links with seasonal rainfall characteristics other than ADWP.

The adverse effect of stormwater pollution in the receiving water bodies and the necessity for treatment was recognised in the 1960s (Hallberg, 2007). A number of different treatment techniques are commonly used for stormwater treatment. For example, detention or retention basins can be used not only for decreasing the pollutant concentration but also for managing stormwater discharge flow rates. Other devices which are based on gravity separation include sediment traps and basins. They will not be effective in the removal of dissolved pollutants. This aspect is especially important for metal removal because a significant fraction of them remains dissolved. For the removal of dissolved and colloidal fractions of organics in highway runoff different types of filter fabric have been used. There are a number of different types of filter media that are used for stormwater treatment. These include sand, coated sand, gravel, crushed glass, perlite, peat, leaf compost, mulch, zeolite, granular activated carbon and other media (Moller et al., 2002; Datry et al., 2003; Liu et al., 2004; Liu et al., 2005; Baltrenas and Brannvall, 2006; Ray et al., 2006). Nonetheless, there are a number of problems and questions which have been raised recently which can be summarised as follows: there are few comparative tests between different media (McLaughlan, 2004). Moreover, runoff generated from different sources is likely to have different physical and chemical properties which might affect the efficiency of the media (Clark et al., 2005).

Thus the objectives of this thesis are: to assess the effects of the seasonal variation, rainfall intensity and ADWP on the metal concentrations in runoff; to analyse the factors affecting their solubility in the runoff and to perform a case study on the treatment SUDS lagoon at a busy test site (J24 M1). These were compared with the metal concentrations found in other natural, agricultural sources and sewage work discharges.

The literature review is in two chapters: Chapter Two presents a review of previously published material related to sources of metals, their concentration and behaviour. Past observations and findings of metal concentrations obtained from highways and residential areas are described but it is shown that such factors as rainfall intensity and duration, traffic flow, climate, antecedent dry weather period (ADWP) and first flush characteristics have no scientific correlations and coordination. The chapter closes with a summary of the knowledge gaps and their impact on the objectives of this research programme.

Chapter Three is devoted to evaluating the potential of filter treatment processes for the enhanced removal of metals from stormwater. The performance of commonly available commercial media, their properties and effectiveness of the treatment are presented. Specific attention has been paid to crushed recycled glass as a potential material for filtration because of its ready availability, which was then investigated later in the thesis. The chapter closes with a summary of these findings of previous research, and gaps and unanswered questions with respect to the concentration and behaviour of metals in stormwater, which arise as a result of the review, are considered. This leads to the objectives, with the intention of answering some of these questions, which then form the basis for designing a research methodology to obtain new data.

Chapter Four presents the methodology of sampling and analysing metals from the different field sites (highway, rural brooks and sewage works). Chapter Five describes the design of the filter unit, followed by the experimental protocol for sampling and analysing metals. Details of the media adsorption studies are also presented.

Chapter Six presents and discusses the results which have been obtained during field work as well as by laboratory study, including filtration and adsorption. The chapter begins with a description of difficulties encountered with experiments. Comparison and contrasts are made with the findings of previous related research as reviewed in Chapter Two.

Chapter Seven presents the conclusions of the study and proposes a plan for future research in this field. Appendices and References are attached at the end of the thesis.

CHAPTER 2

LITERATURE REVIEW ON THE PRESENCE AND BEHAVIOUR OF METALS IN STORMWATER RUNOFF

2.1 INTRODUCTION

Stormwater road runoff contains contaminants that are both dissolved and bound to particulates. Many of these contaminants are potentially hazardous and are likely to have adverse effects on the receiving water bodies. Some previous literature, for example, has suggested that road runoff could contribute up to 75% of total metals to a receiving water body (USEPA, 1996). In future there will be increased attention paid to pollutants derived from road transport, both as a result of the Water Frame Directive (WFD) and as a result of the awareness of transport's major contribution to total environmental emissions.

This review is divided into two subsections: one to cover the sources of metals and the second to examine the reactions and behaviour of metals once in the environment. The major influences on metal concentrations reported in the literature are: season, rainfall intensity, the duration of the antecedent dry weather period (ADWP) and first flush. These data are compared and contrasted between papers and reports.

2.2 SOURCES OF METALS

Urban activities generate pollutants which build up on surfaces throughout the watershed. When rain is precipitated, the pollutants that have accumulated on the surface wash off and flow via the drainage system into the nearest water body. Stormwater runoff volumes in urban areas are higher than in rural areas because of the impervious surfaces. There will be variable amounts of dilution and therefore different environmental effects. Stormwater pollution also comes from point and non-point (diffuse) sources. This study is concerned with diffuse-source pollution from vehicles and roads but data has been presented comparing this with sewage work discharges to compare the relative environmental impact.

Over the past two decades, the term “heavy metals” has been widely used by different authors in their publications and even in legislation related to their potential harmful effects (toxicity and ecotoxicity). These metals have included cadmium (Cd), chromium (Cr), lead (Pb), copper (Cu), mercury (Hg), nickel (Ni) and zinc (Zn). There is no authoritative definition of heavy metals to be found in the ISO, EU, Environment Agency or Highway Agency environmental codes. As a consequence, this term has been used inconsistently, which has resulted in confusion about the meaning and therefore difficulty in accessing relevant papers through their titles. For example, the term “heavy metals” has also been applied to semi-metals (metalloids) such as arsenic (As).

Duffus (2002) conducted a thorough review of current usage of the term “heavy metals”. His detailed list of 38 definitions, taken from different sources, was compiled in order to demonstrate that those definitions had no precise chemical meaning. He concluded that “… the term “heavy metals” is both meaningless and misleading” (Duffus, 2002, p.794) and “…the term “heavy metal” has never been defined by any authoritative body such as IUPAC” (Duffus, 2002, p. 804). To avoid this confusion he suggested classifying the impact of metals on the environment on the basis of their chemical properties. This could help to indicate the toxicity of metal species. The experimental studies conducted by Duffus were focused on the potential toxicity of metals and their compounds, which could be understood and assessed by their solubility and consequently bioavailability. The latter, however, also depends on biological factors such as take-up mechanisms and also on the interactions in surface waters to form, for example, organic ligands. Metallic elements were then simply classified by their position in the periodic table.

It is now widely recognised that highway runoff is one of the main contributors of metals to the environment. The toxicity of trace elements to a given species may vary according to the water hardness. The toxicity of metals varies over a wide range depending on the concentration of Ca. Appendix 2 contains a table with different concentration limits for zinc, copper and iron for different levels of water hardness.

Table 2.1 summarises some current, general information about vehicular sources of metals. The data in the table suggests that the primary sources of these key metals are the friction components, namely brakes and tyres. It is also possible to make other suggestions. One is that vehicle corrosion is not an important source of pollution although another explanation is that few have investigated these metals; iron, for example, has not been of interest because of its low toxicity.

Table2.1 Vehicular sources of selected metals (number refers to reference source)

	Pb	Zn	Cu	Cr	Cd	Ni	Fe
Wear of vehicles' tyres and brake pads	2; 3; 6	1; 2; 3; 4; 5; 6	1; 2; 3; 4; 5; 6; 7		1; 3	7	6
Corrosion of metal objects							
Petrol additives	1						
Lubrication oil		5			1		
Metal processing industry			1	1	1	1	
Hydrocarbon combustion	2				2		
Catalytic converter			2				
Diesel		2; 4	4		4	4	

1 - Makepeace (cited in Nouh, 2001); 2 - Chocat (cited in Dechesne et al., 2004); 3 - Davis et al., 2001; 4 - Weckwerth ,2001; 5 – Harrison et al., 2003; 6 - Davis and McCuen, 2005; 7 - Prestes et al., 2006.

A second conclusion from this summary of the literature is that little work has been done on spills and leaks of fuels and fluids. Lead in petrol is the exception. There has been no lead in petrol in Europe since 1990 but it is still allowed in other regions of the world. A number of studies (Makepeace [cited in Nouh, 2001]; Menkes and Fawcett, 1997; [Lead in gasoline – international pattern of use, n.d.]) present data about lead in petrol including the extent of use and sales. Studies between 1960 and 1970 (see Menkes and Fawcett, 1997) had demonstrated that the lead contained in gasoline was released into the environment, which was potentially hazardous, and policies were developed to reduce and eliminate lead in fuel. Hence, the amount of lead released into the atmosphere in Europe and USA has decreased sharply (O'Neill, 1998; Weckwerth, 2001; Harrison et al., 2003).

Similar results have been reported for water bodies. For example, Mosley and Peake (2001) have noted and concluded that Pb levels are continuing to decline in urban stormwater because of its exclusion from petrol. Lead salts are poorly soluble and the rate of decline in storm water could be a potential indicator of the importance of solids and their size in flushing pollutants from the environment. Nonetheless, this problem still exists in some developing countries. For example, it has been concluded that in Curitiba (Brazil) the annual load of Pb derived from highways was greater than some other metals (0.5 kg/ha•year), compared to copper (Cu) (0.31 kg/ha•year) and cadmium (Cd) (0.008 kg/ha•year) (Prestes et al., 2006). Unfortunately this study did not provide any information about other, non-vehicular sources of lead.

When studying pollution problems in Lagos, Nigeria, Ajibola et al. (2005) observed Pb inputs from a range of anthropogenic sources such as industrial and sewage effluents but they excluded traffic and highways. Unfortunately, the paper does not include enough information about either phase to which Pb was analysed or the analytical technique applied in this study, all of which makes further interpretation of their results unconvincing. Leaded petrol is still sold in Nigeria (Asia et al., 2006) and, taking into account the data from Brazil, for example, it is likely that traffic is a major source of lead.

Hardiyanto and Guzman (2008) found both Pb and Cd in white cabbage grown along a main road in Indonesia and pointed out that the source of these metals could be leaded petrol. Pb can accumulate in the soil and in the roots of vegetables, which is also attributable to the use of Pb-contaminated water for irrigation purposes (in this study the level of the total Pb in irrigation water was 0.12 mg/l). The maximum concentration (rather than mean values) of Cd in the two studied areas was 0.42 µg/g of d.w. and 0.75 µg/g of d.w. with 7680 vehicles per day. The same opinion about the various origins of Pb was expressed by Muwanga and Barifaijo (2006). Moreover, they also ascribed the presence of Pb to other sources, such as slag used as a sub-base for road buildings and left on industrial sites. Cd and Pb are two of the most toxic metals used in vehicles but other less toxic metal emissions are also present (Table 2.1) and these may still represent a hazard if they accumulate.

Fig. 2.1 represents the proportions of the metals reportedly derived from each of the three major sources: tyre wear, brake wear and the roofs of buildings:

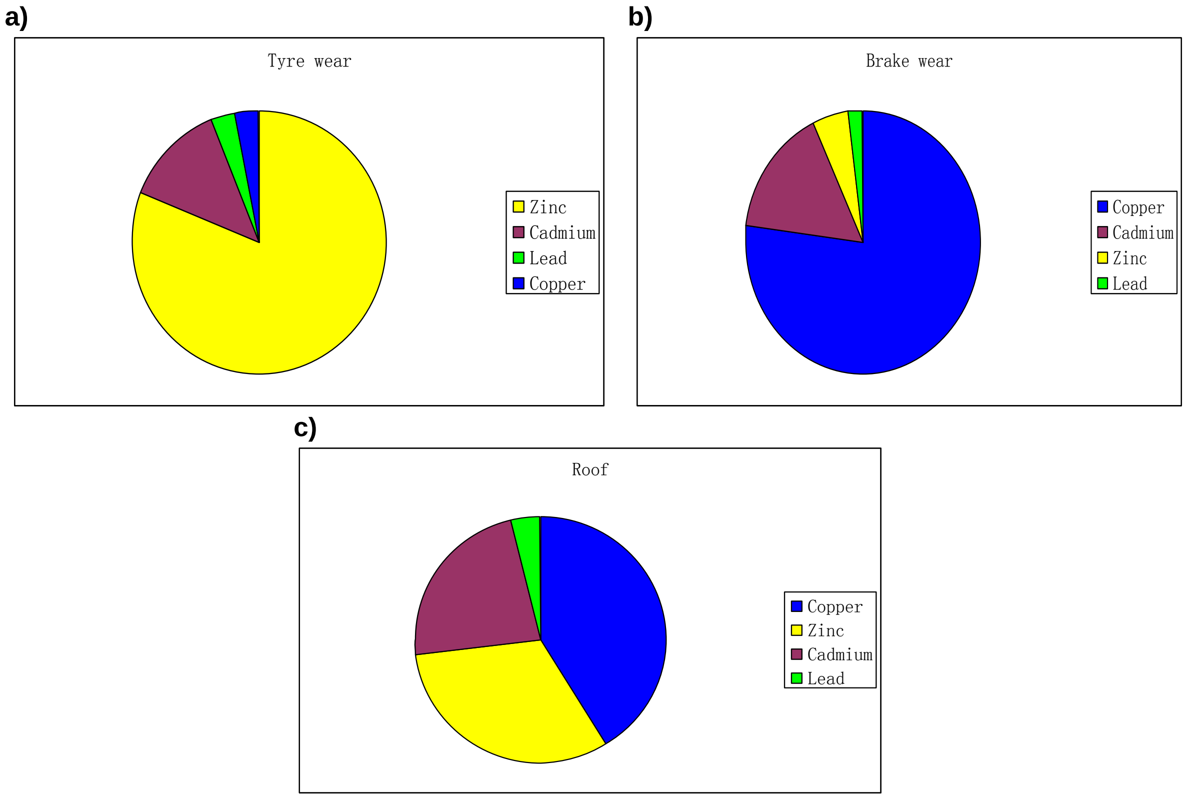

Fig. 2.1 Sources of metals (adapted from Davis et al., 2001)

From these figures it is apparent that brake emissions from vehicles were the major source of copper. Brake linings were indicated as the major contributor of both particulate and soluble copper (Weckwerth, 2001).

Zinc was deposited as a result of tyre wear. By simultaneously measuring the size of copper and zinc particles in the aerosol samples (Weckwerth, 2001) it was shown that that the Zn concentration in the fine fraction (< 2.5 um) was 2-3 times higher compared to the coarse fraction. It was concluded therefore that the main proportion of Zn was derived from the condensation and re-precipitation of volatile fine particles containing Zn rather than directly from tyre debris. Another study was conducted by Harrison et al. (2003) which suggested that the fine particles of Zn arose from engine exhaust or from other high-temperature non-traffic sources, rather than tyres. Washoff from roofs and street furniture was also found to be a major contributor to zinc and copper levels (Davis and McCuen, 2005).

2.3 POLLUTANT LEVEL DETERMINATION IN RUNOFF

Interpretation of pollution concentration data from highway runoff is a complex problem involving as it does weather conditions, environmental interactions and the type of highway. Some previous work has addressed this problem of obtaining representative and reproducible samples (Lee et al., 2010). The results reported in the literature are also based on a number of different measurement and analytical techniques. However, numerical modelling of the input can be more difficult because of the variability and unpredictability in the magnitude and frequency of rainfall events. This, therefore, complicates calculations of mass in the runoff.

2.3.1 Grab Sample Measurements

The most convenient, simplest and least costly water quality measurements have been conducted through ‘grab samples’ taken at various times during a rainfall event. Grab samples provide only an instantaneous measurement, but a series of grab samples can be used to obtain a pollutograph, i.e. to plot a curve that represents the pollutant concentration during a whole rainfall event. For example, this type of sampling programme has been used to identify the ‘first flush’ (Lee et al., 2004). Lee et al. (2004) hypothesised that when metal behaviour was being studied, such as the distribution between dissolved and particulate forms of a metal, then composite samples may age and disguise the original speciation present at sample collection. Grab samples were also shown to be useful in describing flow behaviour and concentration dynamics (pattern) by Wong et al. (1997).

Some authors consider that a limited number of grab samples may be used when providing an indication of pollutant concentration during dry weather when conditions are at steady state. They can also be useful for investigating long-term water quality trends, when it would be possible to take a large number of samples over several years and seasons. One of the main drawbacks of collecting grab samples, however, is that a large number of samples may be needed to provide adequate statistical information about the pollutant load carried by runoff (Davis and McCuen, 2005).

2.3.2 Composite Sample Measurements

Flow composite sampling enables more precise analysis to be conducted and a better understanding of the mass of pollutants transported in runoff to be achieved. In this way, it is not only the concentrations of pollutants that are measured (as in the case of grab samples), but information is also obtained about the variations in flow rate. This composite parameter, which is known as event mean concentration (EMC), is defined as the pollutant load washed off by a rainfall event divided by the event runoff volume (Davis and McCuen, 2005):

$$EMC = \frac{\sum_{i=1}^{n} C_i Q_i \Delta t_i}{\sum_{i=1}^{n} Q_i \Delta t_i} \qquad (2.1)$$

where C_i is the individual measurement of the concentration; Q_i is the flow rate at the time concentration C_i was measured and Δt_i denotes the time intervals associated with C_i measurements.

There are also automatic samplers which can be programmed not at flow intervals but at time-based intervals. However, Poissant and Beron (1992), analysing rainfall events in Montreal, found that while observing rainfalls with low intensities, there is a risk that the time between two samples might be too small to collect a sufficient volume for chemical analysis. On the other hand, with rainfalls of high intensities, bottles might easily overflow.

One of the conclusions of this thesis (see Chapter 7.0) is devoted to sampling procedure and it is inferred that for the analysis of metals, especially in their dissolved forms, grab sampling could be more effective, although it is laborious.

2.4 METALS IN HIGHWAY AND URBAN RUNOFF

Table 2.2 summarises some previous work selected to demonstrate metal concentrations found in highway and urban runoff. The shaded rows represent runoff from residential and commercial areas as opposed to trunk roads. Analysis of the data in the table suggests that the level of metals will depend on a number of key factors which are summarised in Table 2.3 and described in detail in this chapter.

Table 2.2 Concentrations of some metals in highway and urban runoff and digestion procedure for total metal recovery

Metal	C_{tot}, ppm	C_{dis}, ppm	f_{dis}	TSS, ppm	Number of vehicles/day	Catchment area description	Sampling technique	Digestion procedure	Metals' analyser	Reference
Fe	0.1	Not defined	**-**	Not clearly defined	Not defined	Three sites with area 936; 1.120; 1.170 m^2.	Grab samples	Not defined	ICP-MS	Maniquiz et al., 2009
	3.419	0.211	0.064	86.9	Urban runoff	170 ha	Grab samples were collected by hand	Hot plate (2mL of HNO_3)	GFAAS; ICP-AES	Mosley and Peake, 2001
	8.0	Not defined	-	Not defined	450-45000	Residential and commercial areas	Self-sealing sampler fixed next to a road	Acid digestion	ICP-OES	Apul et al., 2010
summer	1.03 – 19.3	0.017 – 0.058	0.017 -0.003	14 - 520	120000	13,700 m^2; 9 events	Samples were collected when the flow exceeded 1 m^3/hr for every volume of 4 m^3	Not defined	ICP-SFMS	Hallberg et al., 2007
winter	0.41 – 226	0.01 – 0.017	0.024 -8*10^{-5}	13 - 4800						
Pb	0.02	Not defined	-		Not defined	Three sites with area 936; 1.120; 1.170 m^2		Not defined	ICP-MS	Maniquiz et al., 2009*
	~ 0.030	~ 0.0008	0.027	~ 50	9000	1.300 m^2.	Grab samples were collected by hand	Microwave digestion	DPASV	Prestes et al., 2006
	0.023	Not defined	-	114.58	23647 – 83579	6 sites; 60 events: 4133 – 58600 m^2.	Not defined	Not defined	Not defined	Crabtree et al., 2006
	0.038	0.0038	0.1	243.87	5000 - 200000	30 sites; 340 events	Not defined	Not defined	Not defined	Crabtree et al., 2008
	0.016/0.154	0.0008/0.0009	0.05/0.006	61/517	20000	2000 m^2; winter/thawing	Not defined	Not defined	Not defined	Frimmel et al., 2007
	0.042	0.002	0.048	226.9	Runoff from the site for handling and storage oil products	1200 m^2 covered by asphalt	Samples were collected at 5 min frequency	Not defined	Not defined	Berretta et al., 2008
	0.113	Not defined	-	425	18000	2300 m^2	Samples were taken both by sampler and manually. Bubbler flow meter was installed.	Not defined	Not defined	Dierkes et al., 2008
	0.036	0.003	0.08	86.9	Urban runoff	170 ha	Grab samples were collected by hand	Hot plate (2mL of HNO_3)	GFAAS; ICP-AES	Mosley and Peake, 2001
	Not defined	0.013/0.005	-	140/19	Road runoff/ roof runoff	University of Genoa; 2800 m^2	Automatic sampler; samples were collected at 5 min intervals	-	Not defined	Gnecco et al., 2005
	0.12	Not defined	-	Not defined	6240 - 7680	Road along white cabbage plantation	Grab samples	Hot plate (5 mL of HNO_3)	AAS	Hardiyanto and Guzman, 2008
	0.08	Not defined	-	Not defined	450-45000	Residential and commercial areas	Self-sealing sampler fixed next to a road	Acid digestion	ICP-OES	Apul et al., 2010

Continuation of **Table 2.2**

Metal	**C_{tot}, ppm**	**C_{dis}, ppm**	**f_{dis}**	**TSS, ppm**	**Number of vehicles/day**	**Catchment area description**	**Sampling technique**	**Digestion procedure**	**Metals' analyser**	**Reference**
Pb	0.14	Not defined	-	762	25755	14184 m^2 kerb and gully; 42 events	Samples were collected proportionally to volume of runoff passing the measuring section which was determined experimentally	Not defined	AAS	Desta et al., 2007
summer	0.002 – 0.05	$9*10^{-5} – 2*10^{-4}$	0.045 –0.004	14 - 520	120000	13,700 m^2 ; 9 events	Samples were collected when the flow exceeded 1 m^3/hr for every volume of 4 m^3	Not defined	ICP-SFMS	Hallberg et al., 2007
winter	0.001 – 0.296	$9*10^{-5} – 1.7*10^{-4}$	$0.09 - 6*10^{-4}$	13 - 4800						
Cd	0.003	Not defined	-		Not defined	Three sites with area 936; 1.120; 1.170 m^2	Grab samples	Not defined	ICP-MS	Maniquiz et al., 2009
	~ 0.0015	traces	-	~ 50	9000	1.300 m^2.	Grab samples were collected by hand	Microwave digestion	DPASV	Prestes et al., 2006
	0.0005	Not defined	-	114.58	23647 – 83579	6 sites; 60 events: 4133 – 58600 m^2.	Not defined	Not defined	Not defined	Crabtree et al., 2006
	0.00063	0.00026	0.41	243.87	5000 - 200000	30 sites; 340 events	Not defined	Not defined	Not defined	Crabtree et al., 2008
summer	$4*10^{-5} – 2*10^{-4}$	$3*10^{-5} – 5*10^{-5}$	0.85 – 0.25	14 - 520	120000	13,700 m^2 ; 9 events	Samples were collected when the flow exceeded 1 m^3/hr for every volume of 4 m^3	Not defined	ICP-SFMS	Hallberg et al., 2007
winter	$6*10^{-4} – 0.002$	$1.5*10^{-4} – 2*10^{-4}$	0.25 – 0.1	13 - 4800						
Cu	0.12	Not defined	-	762	25755	14184 m^2 kerb and gully; 42 events	Samples were collected proportionally to volume of runoff passing the measuring section which was determined experimentally	Not defined	AAS	Desta et al., 2007
	0.1	Not defined	-	Not defined	450 – 45000	Residential and commercial areas	Self-sealing sampler fixed next to a road	Acid digestion	ICP-OES	Apul et al. 2010
summer	0.006 – 0.221	0.002 – 0.023	0.34 – 0.104	14 - 520	120000	13,700 m^2	Samples were collected when the flow exceeded 1 m^3/hr for every volume of 4 m^3	Not defined	ICP-SFMS	Hallberg et al., 2007
winter	0.005 – 1.216	0.002 - 0.023	0.4 – 0.019	13 - 4800						

Continuation of **Table 2.2**

Metal	C_{tot}, **ppm**	C_{dis}, **ppm**	f_{dis}	**TSS, ppm**	**Number of vehicles/day**	**Catchment area description**	**Sampling technique**	**Digestion procedure**	**Metals' analyser**	**Reference**
Cu	0.2	Not defined	-	Not clearly defined	Not defined	Three sites with area 936; 1.120; 1.170 m^2	Grab samples	Not defined	ICP-MS	Maniquiz et al., 2009
	0.041	0.021	0.51	114.58	23647 – 83579	6 sites; 60 events: 4133 – 58600 m^2.	Not defined	Not defined	Not defined	Crabtree et al., 2006
	0.091	0.031	0.34	243.87	5000 - 200000	30 sites; 340 events	Not defined	Not defined	Not defined	Crabtree et al., 2008
	Not defined	0.011	-	32	More than 30000	A74 (M)	Not defined	-	Not defined	McNeill and Olley, 1998
	0.153/0.83	0.023/0.064	0.15/0.08	61/517	20000	2000 m^2	Not defined	Not defined	Not defined	Frimmel et al., 2007
	0.072	0.025	0.35	226.9	Runoff from the site for handling and storage oil products	1200 m^2 covered by asphalt	Samples were collected at 5 min frequency	Not defined	Not defined	Berretta et al., 2008
	0.279	Not defined	-	425	18000	2300 m^2	Samples were taken both by sampler and manually. Bubbler flow meter was installed.	Not defined	Not defined	Dierkes et al., 2008
	0.023	0.01	0.43	86.9	Urban runoff	170 ha	Grab samples were collected by hand	Hot plate (2mL of HNO_3)	GFAAS; ICP-AES	Mosley and Peake,2001
	Not defined	0.019/0.010	-	140/19	Road runoff/ roof runoff	University of Genoa; 2800 m^2	Automatic sampler; samples were collected at 5 min intervals	-	Not defined	Gnecco et al., 2005
Ni	0.025	Not defined	-	Not clearly defined	Not defined	Three sites with area 936; 1.120; 1.170 m^2	Grab samples	Not defined	ICP-MS	Maniquiz et al., 2009*
	0.005	Not defined	-	114.58	23647 – 83579	6 sites; 60 events: 4133 – 58600 m^2.	Not defined	Not defined	Not defined	Crabtree et al.,2006
	0.010	Not defined	-	243.87	5000 - 200000	340 events; 30 sites	Not defined	Not defined	Not defined	Crabtree et al.,2008
	0.011/0.042	0.0083/0.0067	0.75/0.16	61/517	20000	2000 m^2; winter/thawing	Not defined	Not defined	Not defined	Frimmel et al., 2007

Continuation of **Table 2.2**

Metal	**C_{tot}, ppm**	**C_{dis}, ppm**	**f_{dis}**	**TSS, ppm**	**Number of vehicles/day**	**Catchment area description**	**Sampling technique**	**Digestion procedure**	**Metals' analyser**	**Reference**
Ni	0.256	0.075	0.29	226.9	Runoff from the site for handling and storage oil products	1200 m^2 covered by asphalt	Samples were collected at 5 min frequency	Not defined	Not defined	Berretta et al. (2008)
	0.03	Not defined	-	Not defined	450 – 45000	Residential and commercial	Self-sealing sampler fixed next to a road	Acid digestion	ICP-OES	Apul et al. 2010
summer	10^{-4} – 0.015	Not clearly defined	-	14 - 520	120000	13,700 m^2; 9 events	Samples were collected when the flow exceeded 1 m^3/hr for every volume of 4 m^3	Not defined	ICP-SFMS	Hallberg et al. (2007)
winter	$7*10^{-4}$ – 0.151	Not clearly defined	-	13 - 4800						
Cr	0.006	Not defined	-	Not clearly defined	Not defined	Three sites with area 936; 1.120; 1.170 m^2	Grab samples	Not defined	ICP-MS	Maniquiz et al. 2009
	0.007	Not defined	-	243.87	5000 - 200000	340 events; 30 sites	Not defined	Not defined	Not defined	Crabtree et al. (2008)
	0.011/0.071	0.0016/0.0104	0.15/0.15	61/517	20000	2000 m^2; winter/thawing	Not defined	Not defined	Not defined	Frimmel et al., 2007
summer	0.0016 - 0.045	Not clearly defined	-	14 - 520	120000	13,700 m^2; 9 events	Samples were collected when the flow exceeded 1 m^3/hr for every volume of 4 m^3	Not defined	ICP-SFMS	Hallberg et al. (2007)
winter	0.057 – 0.366	Not clearly defined	-	13 - 4800						
Pt	0.004	Not defined	-	114.58	6 sites; 60 events: 4133 – 58600 m^2.	Not defined	Not defined	Not defined	Not defined	Crabtree et al. (2006)
Pl	0.0004	Not defined	-	114.58	6 sites; 60 events: 4133 – 58600 m^2.	Not defined	Not defined	Not defined	Not defined	Crabtree et al. (2006)

Continuation of **Table 2.2**

Metal	C_{tot}, **ppm**	C_{dis}, **ppm**	f_{dis}	**TSS, ppm**	**Number of vehicles/day**	**Catchment area description**	**Sampling technique**	**Digestion procedure**	**Metals' analyser**	**Reference**
Zn	0.2	Not defined	**-**	Not clearly defined	Not defined	Three sites with area 936; 1.120; 1.170 m^2	Grab samples	Not defined	ICP-MS	Maniquiz et al. 2009*
	0.140	0.057	0.41	114.58	23647 - 83579	6 sites; 60 events: 4133 – 58600 m^2	Not defined	Not defined	Not defined	Crabtree et al. (2006)
	0.352	0.112	0.32	243.87	5000 - 200000	340 events; 30 sites	Not defined	Not defined	Not defined	Crabtree et al. (2008)
	0.029	Not defined	-	32	More than 30000	A 74 (M)	Not defined	Not defined	Not defined	McNeill and Olley (1998)
	0.296/1.721	0.231/0.288	0.78/0.16	61/517	20000	2000 m^2; winter/thawing	Not defined	Not defined	Not defined	Frimmel et al., 2007
	0.68	Not defined	-	425	18000	2300 m^2	Samples were taken both by sampler and manually. Bubbler flow meter was installed.	Not defined	Not defined	Dierkes et al. (2008)
	0.415	0.055	0.13	226.9	Runoff from the site for handling and storage oil products	1200 m^2 covered by asphalt	Samples were collected at 5 min frequency	Not defined	Not defined	Berretta et al. (2008)
	0.279	0.131	0.47	86.9	Urban runoff	170 ha	Grab samples were collected by hand	Hot plate (2mL of HNO_3)	GFAAS; ICP-AES	Mosley and Peake (2001)
	Not defined	0.081/0.447	-	140/19	Road runoff/ roof runoff	University of Genoa; 2800 m^2	Automatic sampler; samples were collected at 5 min intervals	-	Not defined	Gnecco et al (2005)
	0.12	Not defined	-	Not defined	450 - 45000	Residential and commercial	Self-sealing sampler fixed next to a road	Acid digestion	ICP-OES	Apul et al. (2010)
	0.66/0.07	0.04/0.05	0.061/0.72	762/49	25755/18429	14184 m^2 (kerb and gully)/ 9600 m^2 (filter drain); 42 events	Samples were collected proportionally to volume of runoff passing the measuring section which was determined experimentally	Not defined	AAS	Desta et al. (2007)
summer	0.023 – 0.643	0.008 – 0.12	0.35 – 0.19	14 - 520	120000	13,700 m^2; 9 events	Samples were collected when the flow exceeded 1 m^3/hr for every volume of 4 m^3	Not defined	ICP-SFMS	Hallberg et al. (2007)
winter	0.021 – 5.71	0.008 – 0.12	0.35 – 0.02	13 - 4800						

The UK Highways Agency suggests that the main factors affecting metal concentration in runoff are traffic flow, climate, antecedent dry weather periods (ADWP) and rainfall characteristics (Crabtree et al., 2006; Crabtree et al.,2008). Analysis of the literature presented here suggested that the sampling procedures and analytical techniques employed are also important. Our research data (see section 6.1) confirmed this by showing that the digestion procedure used for metal recovery affected total metal concentrations and consequently the ratio of the dissolved fraction of the metals $\boldsymbol{f_{dis}}$. This had not been discussed in the literature previously and it is analysed further in this chapter (section 2.7.2).

Most of the studies also failed to define precisely the methods used for sample collection or the preparation and analysis of metals. In the majority of studies a hot plate was used for total metal recovery, apart from Prestes et al. (2006), where microwave digestion was used. One of the conclusions of this thesis (Chapter 7.0) is that this could potentially be a problem when chemical and eco-toxicity data are interpreted. An objective of this thesis was thus to identify suitable analytical methods for measuring the concentration of metals in relation to their mobility in the environment (soluble and total speciation).

Table 2.2 also shows that there is little information about Fe, due to its low toxicity (EQS for Fe_{dis} = 1mg/l) (Council of European Communities, 1976), even though the literature has suggested that Fe will occur in comparatively high concentrations in urban runoff compared to copper and zinc as a result of vehicle wear and its general usage (Davis and McCuen, 2005).

Table 2.3 Key factors affecting metal analysis results

Rainfall characteristics	Type of area	Digestion procedure	Metal analyser
• ADWP • rainfall intensity and duration	• highway • urban	• hot plate •microwave digestion	• ICP; ICP-MS • GFAAS

The toxicity of the other metals listed is more of a problem. They will be toxic at lower concentrations to humans, plants or invertebrates. For example, the usual indicators of metals in highway runoff are Cu and Zn, as noted above (section 2.2). One can see (Table 2.2) that the concentration ranges for these metals are wide

(Crabtree et al., 2006; Crabtree et al., 2008; Dierkes et al., 2008). The study conducted by Frimmel et al. (2007) showed that snow and the consequent runoff as it thawed gave the highest metal concentrations by comparison with rain runoff, even though the area under investigation did not experience a high level of automobile use (20,000 vehicles per day, compared to 120,000 at the M1 test site). A possible explanation, as suggested by this thesis (section 6.2), is that the de-icers or the high temperature fluctuations cause accelerated corrosion but neither of these was noted by the author.

It can be noted from Table 2.2 that the values of pollutants reported in these works depended on the location of the sampling points. Thus, in some cases, pollutant concentrations were measured after the runoff had passed through a pre-treatment system (Mosley and Peake, 2001; Prestes et al., 2006), although the type of system was not always clearly defined. In some cases, the values quoted pertain to runoff after it had undergone more complex treatment, such as in an interceptor and lagoon (CIRIA, 2000; Crabtree et al., 2006). Crabtree et al. (2006) made a comparison of metals, relating PAH and TSS removal to different types of treatment system, including oil separator/lagoon, oil separator/dry balancing pond or ditch with filter drain and oil trap manhole/sedimentation tank. The best pollution removal efficiency was observed with a combination of a bypass oil separator and a lagoon. Thus, for example, TSS values decreased 37% after the oil separator and 36% after the wet balancing pond. The oil trap manhole did not show any effectiveness in TSS removal, while the sedimentation tank provided 41% removal of metals affiliated with TSS particles. However, the sedimentation tank did not perform well in terms of PAHs removal. The dry balancing pond demonstrated poor reduction of metals (only 12%). This paper was the only one which showed the importance of defining the place of sampling as well as the type of treatment system used.

The data obtained (Gnecco et al., 2005) from road runoff indicated higher metal concentrations than other diffuse sources of stormwater, for example, roof runoff. The exception to this could be zinc, which on occasions had a much higher concentration in roof runoff compared to road runoff. Gnecco et al. (2005) reported the highest concentration of Zn of all the reported studies and this was due to the wash-off of corrosion particles from galvanised roofs or zinc gutters.

2.5 METALS IN TREATED SEWAGE

Estimates of all the metal inputs into an environmental area or catchment are rarely found in the literature. Within most catchments sewage or industrial effluent treatment works represent an identifiable point source, even though the sewage work effluents will integrate contributions from a number of sources in the catchment. For example, in the UK, at least, the contents of most sewerage systems are combined with runoff from urban roads, industrial effluents and domestic waste water. Therefore, sewage work effluents have been studied more than the other potential inputs; for example, no literature was found on metals from diffuse agricultural sources, even though artificial fertilizer and animal wastes are known to contain metals. Most work is confined to sludges and slurry. There is also very little information on the inputs from minor rural roads and navigation canals, although problems with the tin and copper used to protect boats have been reported (Matthiessen et al., 1999). Discharges to sewers from industrial processing are regulated, monitored and reported but an analysis of this contribution was beyond the scope of this thesis.

Bubb and Lester (1995), for example, suggested that under normal flow conditions sewage effluent could average between 2 and 20% of the total volume of many UK rivers but under dry weather flow conditions sewage effluent can constitute up to 100% of the flow. This dilution is crucial to the toxicity and the achievement of the EQS (Veen et al., 2002). This literature review, therefore, has shown that there is a scarcity of data concerning the amount *(proportion)* of metals in surface waters that is derived from the following three sources: sewage work effluents, urban and agricultural runoff. An objective of this thesis was thus to compare metal concentrations in treated sewage with the concentrations obtained from the M1 in order to identify the major source of metals in the catchment. The same opinion about the lack of data was expressed by Sweeney and Saundo-Wilhelmy (2004) who noted that there had been almost no previous information on the sources of metals in sewage effluent in the USA. They reported that the most recent studies, conducted before their own research, had been devoted to Hg levels in the New York catchment area. No measurements of the other potentially hazardous metals had been obtained prior to theirs.

Table 2.4 summarises selected, relevant findings from recent works on metals found in treated sewage. On analysing the table some trends become apparent. The ranges of key metals, i.e. Fe_{tot} (0 – 0.4 mg/l), Cu_{tot} (0.008 – 0.33 mg/l) and Zn_{tot} (0.01 – 0.27 mg/l), are quite similar to those reported from highway runoff (Table 2.2). There is usually a combination of sources of metal pollutants in natural water. Matthiessen et al. (1999), for example, conducted research on the potential sources and effects of copper and zinc in Essex and Suffolk river estuaries. It was concluded that some sewage work effluents contributed a significant proportion of these metals, although the largest source was always the boating traffic. In this case antifouling paints were responsible for copper and sacrificial anodes for zinc. However, it was also recognised in the paper that it was a challenge to define the precise share of the pollutants deriving from sewage treatment works because of the coincidence of urban sampling stations *(sources)*. Many sewage work outfalls were in the same vicinity as harbours and boat moorings and direct surface runoff drains.

Karvelas et al. (2003) also attempted to analyse possible sources of metals in sewage. They found that Fe was in the highest concentration, followed by Zn, which might have implied specific sources of these elements (e.g. pipe work, corrosion protection and cosmetics). The authors concluded that the proportion of metals removed during the different stages of the treatment process depended on their solubility. The distribution of metals between their total and dissolved forms varied according to the metal in question; for example, more than 80% of Ni was in its dissolved form and more than 90% of Pb in its bound, insoluble form. Karvelas et al. (2003) also concluded that most of the Cu ended up in the sludge (~70%), whereas 63% of Fe remained in the treated effluent. The other metals analysed showed a more even distribution, with 50% of their daily input to the sewage works being present in the sludge and the other 50% being released with the final effluent. However, the calculations were made on the assumption that there were no losses by volatilization. This work would have been even more valuable to the

Table 2.4 Concentrations of some pollutants in treated sewage

Pollutant, mg/l	Measured values, mg/l							
	Karvelas et al.,2003	Kim et al., 2002	Matthiessen et al., 1999	Emongor et al., 2005	Bond, 2001	Bubb and Lester, 1995	Sweeney and Sanudo-Wilhelmy, 2004	Muwanga and Barifaijo, 2006
TSS	12.0	< 30	No data	56.0	< 25	4.2 3.6	No data	No data
Cu tot	0.033	0.07 – 0.33	No data	No data	0.008 – 0.036	0.0173 0.029	No data	No data
Cu dis	0.010	No data	0.005 – 0.02	No data	No data	0.0146 0.009	0.0014	0.01 0.02
Cr tot	0.02	0 – 0.064	No data	No data	0.005 – 0.009	No data	No data	No data
Cr dis	0.002	No data	No data	No data	No data	No data	No data	Less than 0.01 Less than 0.01
Fe tot	0.38	0 – 0.116	No data	0.623	No data	0.06 0.14	No data	No data
Fe dis	0.152	No data	No data	No data	No data	0.041 0.042	No data	No data
Ni tot	0.043	0.42 – 0.87	No data	No data	<0.005	No data	No data	No data
Ni dis	0.034	No data	No data	No data	No data	No data	No data	0.05 0.13
Pb tot	0.027	No data	No data	No data	No data	0.00185 0.00245	No data	No data
Pb dis	0.002	No data	No data	No data	No data	0.000075 0.000087	4x10^{-5}	0.22 0.26
Zn tot	0.27	0.10 – 0.56	No data	0.25	0.01 – 0.037	No data	No data	No data
Zn dis	0.054	No data	0.01– 0.04	No data	No data	No data	No data	0.02 0.06

Continuation of **Table 2.4**

	Karvelas et al.,2003	Kim et al., 2002	Matthiessen et al., 1999	Emongor et al., 2005	Bond, 2001	Bubb and Lester, 1995	Sweeney and Sanudo-Wilhelmy, 2004	Muwanga and Barifaijo, 2006
Sewage work capacity, m^3/day	120000 – 150000	Not defined	500 – 53000	40000	343 – 2881	11124 (mean)/9500 (DWF) 5566 (mean)/4700 (DWF)	18 WWTP 4.4x10^6	Not defined
Sources of metals	Up to 10% - small enterpr.; traffic related pollution	70% - industrial wastewater	Boat traffic; industrial sources	industrial	Not defined	Domestic waste water; metal processing	Domestic wastes and some industrial discharges	Skin and hides factory; spillage from leaded fuel
Treatment process	Activated sludge	Activated sludge	Not defined	Activated sludge	Activated sludge; biological filter; oxidation ditch	Primary sedimentation Percolating filter Primary sedimentation Activated sludge treatment	Not defined	Not defined
Discharging area	Thermaikos Gulf (sea water)	Not defined	Estuaries (mainly sea water)	For irrigation purposes	Not defined	Pix Brook (tribut. of River Ivel) River Ivel (tribute. of River Ouse)	East River (sea water)	Lake Victoria basin
Country	Greece	Singapore	UK	Botswana	UK	UK	USA	Uganda
Digestion technique	Aqua regia (APHA, 1989)	Not defined	Not defined	5 ml of distilled water and HCl followed by 5 ml of HNO_3 (pre-treatment) Water bath ~ 80°C	Not defined	Not defined	Organic extraction	Not applicable
Metals' analyser	AAS and GFA	Perkin-Elmer ICP	Not defined	Microprocessor controlled LED sourced filter photometer	Not defined	AAS	AAS	AAS

objectives of this thesis if the sampling procedure had included information on flow or weather conditions. The observation that the proportion of metals was increased by the first flush of stormwater, as noted later in this chapter, needs to be supported by information from a wider variety of sources.

Bubb and Lester (1995) studied the influence of sewage work effluents on the aquatic environment. Their paper refers to metal concentration data obtained upstream and downstream of the discharge as well as the flow rates of the receiving water. This enabled the analysis of the effect of treated sewage on the river to be performed, taking account of a dilution factor. The average flow rate in the stream (Pix Brook, Letchworth) was obtained from a mass balance equation calculated from the quantity of chloride in the sewage effluent, which was known as a ‘conservative tracer’. The results showed that the Letchworth STW constituted 82.6% of the Pix Brook flow and that it was therefore the major contributor of Cu and Fe. In another case study, however, the dilution capacity of the River Ivel below a STW (Poppy Hill) was impossible to calculate because of a range of tributaries that formed a confluence near the STW. Nevertheless, the data showed that the Poppy Hill STW effluent had a much lower impact on the water environment than the Pix Brook and Letchworth STW. This was explained by the large degree of dilution available in the river compared to the stream. The actual data from this paper is included for comparison with our data in the Discussion section.

The same conclusion concerning dilution can be drawn from the study conducted by Sweeney and Saundo-Wilhelmy (2004). The concentration data presented in their work (see Table 2.4) are low by comparison with previous work, which implies an enormous dilution even in the heavily urbanised area of the East River, New York. The data for Pb concentration showed a distinct high-to-low trend in the East River when compared to the river in the less densely populated area of Long Island Sound (LIS). Other metals such as Cd and Cu did not show this pattern, which suggests that sewage effluents were not the only source of these metals in the relatively suburban LIS. However, the metals measured in this paper were collected from sea water and analysed using liquid-liquid organic extraction, which, as the literature review has suggested, could be another explanation for such low values, apart from massive dilution. These sea water matrices would be expected to demonstrate the effects of a different environment from fresh water and are really beyond the scope of this thesis.

Veen et al. (2002) conducted research into the fate, behaviour and toxicity of copper in sewage effluent after its discharge. Receiving waters were chosen with different levels of hardness (from 100 to 340 mg/l $CaCO_3$) according to the EQS, which allows the permissible level of metals to increase in proportion to water hardness. It was found that the total metal concentration was correlated to the organic matter (DOC concentrations) which was thought to generate ligands for metal binding. Upstream of the sewage work discharge, where the DOC concentration was also lower, such a relationship was not evident. The authors also noted that even after mixing with river water the ligands present in the sewage effluents were resistant to degradation within a 10-day test period. Most rivers in the UK have retention times of less than 5 days. Unfortunately, this paper does not contain any information about the relative flow rates of the receiving water bodies compared to the flow rates of the STWs. If this data had been available, then it would have been possible to calculate the relative contribution by the sewage effluent to the total metal content of the receiving waters. The DOC was conserved and augmented the bioavailability of the copper. Dissolved copper, because of its low reactivity, would be a good tracer for modelling mass balance of dissolved metals in the river.

Another problem encountered with most of the literature reviewed (Bond, 2001; Kim et al., 2002) was that it usually fails to indicate whether the value is measured as total or soluble metal, although in some cases this can be deduced from the analytical techniques reported. Most frequently it was found to be soluble metal because its analysis is much easier to perform. This could be a major flaw in the respective models because in the natural environment there could be a re-adjustment of the equilibrium between the solid and liquid phases.

Despite these limits to the data analysis, the results reported (Table 2.4) demonstrated that given the total volume of sewage discharged (which is 20 M tonnes/day in the UK) and the general similarity in the range of concentrations, those effluents could contribute greater amounts of metals than highway runoff. The environmental impact of the urban sewage works will depend on the dilution available (which itself depends on the location of the sewage works), as well as the proportion of industrial and urban runoff. Kim et al. (2002), for example, reported on sewage which consisted of 70% industrial wastewater (see Table 2.4). The Ni concentration was the highest concentration found in all the literature reviewed of either the treated sewage (Table 2.4) or highway runoff (Table 2.2). The Ni_{tot} was between 0.42 and 0.87 mg/l, which compared with that derived from the runoff from a contaminated industrial site which handled and stored oil products (Berretta et al., 2008; Table 2.2). These results could be anticipated, since the source of these relatively high metal inputs was industry. Total Zn concentrations ranged from 0.10 to 0.56 mg/l (Kim et al., 2002) and, again, these concentrations are typical of industrial activity and result from galvanisation and the presence of cleaning products. The exception to the mean tabulated data from highway runoff was found in the previously mentioned paper by Frimmel et al. (2007) where the thawing snow and ice runoff gave a high total Zn concentration (1.721 mg/l) together with a high TSS of 517 mg/l.

Muwanga and Barifaijo (2006) investigated the impact of urban activities on the Lake Victoria basin and analysed metals in their dissolved forms. The concentrations of all the metals examined, apart from Zn, were also at high values compared to those found elsewhere in the literature and they are summarised separately in Table 2.4. The analysis of this data suggests that the STW does not cope with the pollutants for two possible reasons: firstly, that the STW may be overloaded or, secondly, that some of the units do not work as well as others reported on. A third explanation could be that exceptionally high concentrations of metals are present in the sewage as a consequence of unrestricted discharge from metal processing industries. The paper does not include sufficiently detailed information about the sewage works, for example, about its treatment process or industrial inputs, to make further analysis of the data convincing.

2.6 FACTORS AFFECTING RUNOFF QUALITY PARAMETERS

2.6.1 The First Flush

The term ‘first flush’ has been widely used to describe, manage and alter the treatment practice design relating to stormwater. The first flush of stormwater generates an initial high level of pollutants which need to be dealt with in the first flow of the runoff (Davis and McCuen, 2005). The ‘first flush’ purges pollutants which have accumulated during a dry weather period. The amount of pollutant in this initial flush is thought to be linked to the length of the dry period.

Table 2.5 represents some current definitions of the term “first flush” which were found in the literature. Depending on the field of study, the term can be interpreted in different ways and “first flush” has consequently become a rather loose concept. This problem has arisen because much of the literature does not define the key parameters causing a first flush numerically with, for example, the proportion of total runoff volume, rainfall intensity or ADWP. The evaluation of first flush is likely to be unreliable and unpredictable unless it can be coordinated with the above-mentioned parameters.

Another conclusion from this Table is that the rainfall characteristics and ADWP will vary depending on the region. Thus, for example, the second definition in Table 2.5 describes ‘first flush’ as the seasonal flush experienced after an extended dry period. All of the above-mentioned definitions, however, are based on the fundamental idea that the highest level of pollutants will be observed at the beginning of a rainfall event linked to the amounts of pollutants precipitated during dry weather or low flows. It follows that rainfall intensity will also have its maximum effect at the beginning of rainfall events, which, in terms of obtaining representative samples, might be difficult to pinpoint precisely during a complex storm. Therefore, this may be an explanation for the fact that some authors reported that they had found no indication of a first flush effect for pollutants (Deletic [cited in Davis and McCuen, 2005]), whereas other publications (Mosley and Peake, 2001) provide results in which a first flush of pollutants could be detected. Our results (see section 6.2.1) have added to this discussion by showing that not only are rainfall intensity and ADWP crucial factors affecting the observation of a first flush effect, but also the local conditions of the catchment should be taken into account as well as the phase of individual pollutants.

Table 2.5 Definitions of "first flush"

N	Definition	Source
1.	The delivery of a highly concentrated pollutant loading during the early stages of a storm due to the washing effect of runoff on pollutants that have accumulated on the land.	Calhoun County Departments http://www.calhouncountymi.org/Departments/DrainCommissioner/Definitions.htm
2.	The first big rain after an extended dry period (usually summer) which flushes out the accumulated pollutants in the storm drain system and carries them straight to the ocean.	www.lastormwater.org/WPD/residents/glossary.htm Stormwater glossary
3.	The first flow of water into the stormwater drains after rain. It often contains a lot of pollutants that built up during the dry time before the rain.	Melbourne water www.education.melbournewater.com.au/content/glossary/
4.	The quantity of pollutants, especially nutrients, in water runoff caused by rainfall is higher at the beginning of a storm than later	EPA www.epa.nsw.gov.au/soe/95/28.htm
5.	In a storm event, a first flush (FF) phenomenon occurs when most of the pollution load is transported in the initial part of the event discharged volume.	**First flush pollution load of urban stormwater runoff** Amir Taebi and Ronald L. Droste J. Environ. Eng. Sci./Rev. gen. sci. env. 3(4): 301-309 (2004)
6.	'First flush effects' refers to rapid changes in water quality that occur after early season rains or to the quality of the first flows in a stream. Soil and vegetation particles wash into the streams, sediments on the bed of the creek are stirred up and dissolved substances from soil and shallow groundwater can be flushed into the streams. During this time the electrical conductivity, turbidity and concentration of metals and dissolved ions are higher than usual, pH is often lower. The same type of effects can also follow intense storm events throughout the season.	DEH (2005) *Glossary of Terms*; http://www.deh.gov.au/ssd/glossary/; Australian Government, Department of the Environment and Heritage
7.	The first flush of pollutants in a combined sewer flow has been defined as that part of storm runoff up to the maximum divergence between the dimensionless cumulative percentage of pollutants and the cumulative percentage of flow plotted against the cumulative percentage of time.	Gupta and Saul (1996)
8.	The term "first flush" has been utilised to indicate a disproportionately high delivery of either concentration or mass of a constituent during the initial portions of a rainfall-runoff event.	Sansalone and Christina (2004)

Gnecco et al. (2005) analysed the first flush phenomenon in detail by plotting for each rainfall event a series of partial event mean concentrations (PEMC) versus time. It has been claimed that first flush occurs, when

$$\frac{PEMC(t)}{EMC} \geq 1 \qquad (2.2)$$

This approach allows a numerical comparison to be made between different rainfall events and wash-off processes. This formula was supported by 12 rainfall events observed in the course of their study, when 70% of the storms produced a first flush effect. However, Gnecco et al. (2005) recognised that this formula may be too simple and might not be sufficient if it does not completely represent the whole storm runoff with, for example, pollutant retention below a critical flow rate (the flow rate which is able to wash off the particulate matter) or the situation in the case of a storm with two or more peaks. It is also difficult to evaluate the environmental impact of runoff on receiving water bodies compared to standards: using the dimensionless curves expressed in the equations rather than actual concentration values.

Another analysis was made by Kim et al. (2005) to investigate the nature of the “first flush” depending on storm characteristics. Eight freeway sites in Southern California were studied and, since the sites were small, it was possible to avoid problems associated with runoff travel time that would affect large watersheds. Storm duration, total runoff volume, average rainfall intensity and ADWP were included in the predictive model, which was validated for estimating runoff concentration, description mass loading and EMC. During the experimental monitoring period the behaviour of TSS, COD, oil and grease, turbidity and total phosphorus was evaluated. It was discovered that the fractions of washed-off mass were always higher than the EMC in the first 30% of runoff, which was indicative of a first flush. It was also suggested that rainfall events could then be classified in terms of the three categories of first flush effect (Table 2.6). The main criterion used for first flush evaluation was the fractions of washed-off mass of pollutant. This information and model were useful for estimating the mass load for the design of stormwater treatment equipment, assuming that the traffic volumes can be normalised.

However, despite the fact that rainfall intensity was measured, it was used simply as a collateral factor in the model and unfortunately it went unreported. This missing data may have been useful in helping to generate a more generic mechanistic model.

Table 2.6 First flush categories (modified from Kim et al., 2005)

Categories of first flush	Washed-off mass of pollutants in the first 30% of flow, %
High	more than 50
Medium	30 – 50
Non-first flush	less than 30

In the majority of cases “first flush” has been linked to the TSS. Less information is available for metals or other pollutants, such as organic carbon, N or P. Nevertheless, one study (Prestes et al., 2006) was devoted to investigating the behaviour of metals, including Cu, Pb and Cd. It was found that metals behaved differently in a first flush effect depending on their form (particulate or dissolved). Metals which were associated with particulate matter (Pb and Cd) showed a first flush effect that was linked to TSS, whereas Cu in its total form did not correlate with the first flush of solids. On the contrary, the first flush behaviour was correlated with the dissolved form of copper. Prestes et al. (2006) concluded that the metal concentrations were 3-5 times higher compared with the background concentrations after an ADWP of 10 days or more. Unfortunately, this study did not present any data about rainfall characteristics, although the authors mentioned that there was a period within the rainfall event when runoff was too low to be captured, which implies that the rainfall intensity was a factor affecting the output of pollutants into the water body. These data are important since they are correlated with dissolved and total metals and therefore have implications for this thesis and for effective management practices. However, another problem is that only one rainfall event was taken into account, with the result that there is a lack of replicate information on the effect of different types of storms, a factor that is investigated in this thesis.

Our data (section 6.2.2) confirm the findings from work conducted by Prestes et al. (2006) which support the suggestion that both metal type and solubility are important in first flush effects.

2.6.2 Antecedent Dry Weather Period

An antecedent dry weather period (ADWP) is defined as the time between the end of one rainfall event and the beginning of another. ADWP is an important parameter for predicting stormwater quality. Airborne fall out will also contribute to the accumulated pollutants. The widespread assumption in water quality modelling is that pollutants build up on surfaces throughout the watershed at a constant rate between rainfall events. For example, one of the most common stormwater quality models (Nouh, 2001) estimated the surface pollutant load using the linear, power, exponential or Michaelis-Menton function of the number of dry days. During a rainfall event the accumulated pollutants are washed off from the surface and predicted using this exponential washoff algorithm. The other parameters used in the model will depend on the catchment and surface characteristics. This model has usually been used hitherto only for research purposes rather than for practical design, a limitation which can be explained because of the large number of parameters that are included and needed in this model. The basic principle of time- dependant accumulation has also been included in other simpler models.

Many models have used an empirical power function to relate the pollutant load to the total stormwater runoff volume. The common form can be presented as follows:

$$M = a(V)^b \tag{2.3}$$

where M - event pollution load; V - event runoff volume; *a* and *b* – the coefficients which can usually be determined by the analysis of the concentrations following the plotting of the event load and runoff on a log-log scale.

It is assumed that the longer the ADWP, the greater is the quantity of pollutant deposition and the higher are the consequent concentrations and loadings of pollutants in the runoff. However, the rainfall intensity may also be influential. Thus, some authors did not find any correlation between pollutant load and ADWP (Davis and McCuen, 2005). An explanation for this could be that pollutant load might consist of two components: the basic build-up takes place of pollutants washed off from a surface by typical storms but then additional pollutants could be mobilised during very intensive storms because of surface wash-out (erosion) of the construction materials. The higher the intensity is, the greater the mobilisation of solids; hence, for calculating pollutant load a model may have to include the rainfall intensity as well as ADWP and the type of surface.

2.7 PARTICULATES IN STORMWATER RUNOFF

The literature review has suggested that particulates or suspended solids will be major components in the runoff (Table 2.2). The transport of particles would be a function of velocity, density and particle size distribution (PSD). The fundamental theory suggests that adsorption of metals onto the particle surfaces would occur.

2.7.1 Settling velocity

Most highway runoff treatment systems include a separator if only to catch accidental spills (Crabtree et al., 2006).

Particle size will influence the particle settling velocity and, as a consequence, the efficiency of the separator during the treatment process. Table 2.7 (Faram, 2007) demonstrates the settling velocities for sediments with a density of 2600 kg/m^3 (inorganics such as sand and gravels) for a comparison with the Stokes equation.

Table 2.7 Sediment settling velocities with densities of 2600 kg/m^3 (Faram, 2007)

Size	Settling velocity, cm/sec	Time to settle 1 m
1 mm	12	8 sec
100 µm	0.5	> 3 min
63 µm	0.2	> 8 min
10 µm	0.006	> 4 hrs

Little quantitative research has been found that has investigated the particle size characteristics of runoff. Memon and Butler (2005) monitored rainfall conditions at residential areas in East London and found that predominant size fraction (65% of the total number of particles) was less than 50 µm. It was found, however, that the average particle size increased with the runoff rate. In a similar study of rainfall events in Los Angeles at highway sites with heavy traffic loads (greater than 260,000 vehicles per day), Li et al. (2006) found that more than 90% of the total number of particles had diameters of less than 10 µm. Hergren et al. (2005), on the other hand, took samples from low-traffic residential, commercial and industrial areas and found that the major fraction of particulates in the runoff samples ranged in diameter from 0.45 to 75 µm. These findings are important for the design of treatment facilities, since it is likely that most of the pollutants are attached to the finer particles (Davis and McCuen, 2005), i.e. <10 µm fraction (Table 2.7). Typical treatment methods for fine particle removal are via vegetation in swales and wetlands or by filtration, methods that are examined in this thesis, whereas for coarse particles interceptors, ponds and sedimentation basins can be used (Nouh, 2001).

2.7.2 Chemical Characteristics

One of the important chemical characteristic of metals in the context of this thesis is their ability to affiliate with particulate matter. This affiliation results from sorption reactions between the metals and various inorganic and organic compounds at the surface of the solids. In effluents and receiving waters metals can be classified as being in either of two basic phases (USEPA, 1996), forming part of the particulates or being dissolved in water. These “particulates” include clays and other minerals, humic substances and other poorly defined organic and inorganic ligands. Examples are de-icers and complexes including iron, nitrogen, phosphorus and sulphur compounds.

For example, when analysing different sources of metals (road runoff, STW influent and effluent), Chaminda et al. (2010) indicated that Cu and Zn complexation with DOM depended on the source of organics, which consisted of different types of binding ligands. Total normalised bound concentration had the highest value in samples taken from STW influent. This can be explained by the fact that the most complicated DOM, consisting of proteins, sulphides and other biological components, was found in STW influent. It was shown that Zn and Cu had the weakest binding with DOM originating from road runoff, although urban runoff is derived from road dust which may also contain some synthetic organic ligands. This information has important implications for predicting metal speciation. There is little detailed analysis of the composition of these fine particles or their origin; for example, they may be the products of erosion, anthropogenic fall-out, road construction materials or fluids. This needs further work since they could be important ligands with different affinities for metals.

The literature review has already noted that the ratio between these forms may vary significantly from metal to metal. It could be an important indicator of how to achieve the best treatment performance. This speciation may also change with redox, for example. The total concentration of any metal in water, however, can be expressed as mass per volume and can be written by following the simple USEPA model (1996):

$$C_{tot} = C_{part} + C_{dis}, \tag{2.4}$$

where C_{tot} is the concentration of total metal; C_{part} is the concentration of particulate metal and C_{dis} is the concentration of dissolved metal.

The term 'total metals' refers to the concentration of metals determined in an unfiltered sample after vigorous digestion of the solids. Dissolved metals comprise those metals in an unacidified sample that pass through a 0.45 µm membrane filter (APHA 2005).

The distribution of a metal at equilibrium between the particulate and dissolved forms can be expressed by means of the partition coefficient K_p:

$$K_p = \frac{x}{C_{dis}}, \tag{2.5}$$

where x is the concentration of metals in the particulate phase expressed on a dry weight solid basis (e.g. µg/mg) (USGS, 2000 and APHA, 2005).

Another useful treatability parameter is the dissolved metal fraction f_{dis} which can be defined as

$$f_{dis} = \frac{C_{dis}}{C_{tot}} \tag{2.6}$$

The phase to which a particular metal will partition in a complex environment will depend on other solution characteristics, such as pH, ionic strength, temperature, hardness (base cations), anions, oxidation-reduction potential (redox), the nature and amount of solids and, in some cases, the presence of other elements (Bricker, cited in USGS, 2000). This report presents a review and suggests that metals tend to partition towards the water phase (dissolved) when the following conditions can be observed: low pH, low Eh, low particulate loads and high concentrations of organic matter (Elder, cited in USGS, 2000). By contrast, high pH, high Eh, high particulate loads and non-uniform flow are conditions which result in the binding of metals with particulate matter. Understanding and including these fundamental parameters in a model should allow metal behaviour and the efficiency of metal removal to be predicted. In many natural environments there are complex and antagonistic cross reactions which make these basic predictions more difficult.

The literature review has already noted (section 2.4) that those researchers who have investigated total and soluble metals in runoff obtained very different results. The most recent papers that report on the use of modern analytical techniques, such as ICP, have suggested that there may have been a bias in the earlier data. Duplicate or corroborated research using identical analytical methods, even from different locations, has been rare. In this thesis a comparison is made in section 6.1 among analytical techniques with regard to their potential to influence the results. In most of the literature, for example, in Davis and McCuen (2005) copper, cadmium, chromium and zinc have been found to occur predominantly in the dissolved form, whereas metals such as lead, nickel and iron have been affiliated with particulate matter.

Prestes et al. (2006), when investigating road runoff in a residential area in Curitiba (Brazil) with 9,000 vehicles per day, found a correlation between TSS and Cd and Pb. Cu was found mainly in the dissolved phase. The behaviour of Cd as reported in Prestes et al. (2006) does not agree with the findings elsewhere in the literature (Davis and McCuen, 2005), where the Cd was found to occur predominantly in the dissolved form. It was assumed that this particular experimental area (Curitiba, Brazil) produced its own distinctive sediment which could absorb cadmium or was influenced by the higher concentrations of Pb found in Brazil (Pb is still used in alcohol-augmented petrol). This contradictory result for the behaviour of Cd is important in the context of this thesis which includes a comparison of the potential adsorbents for highway pollutants. Potential adsorbates are reviewed in the next section.

When examining the behaviour of Cu, Fe, Pb and Zn during both dry and wet weather in runoff from roads in residential areas in New Zealand, Mosley and Peake (2001) noted the common pattern of results with their predominance of soluble Cu and precipitated Pb (Davis and McCuen, 2005; Prestes et al., 2006). It was also observed that the Fe and Pb were predominantly attached to solids, whereas the Zn, like Cu, was mainly soluble. Fe, like Pb, was found in the digested solids throughout all types of rainfall events, but Cu and Zn were found in fractions of less than 0.4 µm (soluble; see section 4.2.2) during both dry and wet weather.

There are, however, some studies which show examples of the contrary behaviour. For example, Datry et al. (2003) demonstrated that Zn, Cu, Cr and Cd were mainly in the sediment even when their concentrations in the sediment were high. Datry et al. (2003), however, did not make it clear how mobile the sediment was or, in other words, over what period of time the metals had accumulated. Herngren et al. (2005), examined three types of sites (industrial, commercial and residential) and found that metals such as Al, Fe, Pb and Cr exhibited a strong relationship with TSS in the residential and commercial sites. Cu and Zn, on the other hand, correlated with DOC and TDS. Almost the same situation was observed for the industrial site, with the exception of Cu which showed a completely different behaviour and was highly correlated with TSS. The authors hypothesise that the degree of affiliation between metals and particles might still depend on the source and chemical compositions of the organic matter and competing ions. This complexity in Cu behaviour is very important because its chelation chemistry is more complex, but other studies have not reported on this point. Another important aspect of the work of Herngren et al. (2005) was that the authors used artificial rainwater at their field sites which was prepared with a standard pH and EC.

2.8 DISCUSSION AND RESULTING OBJECTIVES

Previously published research has quantified metals in runoff from highways which originate from traffic activity, with sources including fuel, vehicle exhaust, lubricants, brake materials and tyres. The research reported shows that brake emissions from vehicles are a major source of copper while other metals, particularly zinc, are generated from tyre wear and street furniture and iron results from general vehicle wear. For the total zinc the concentrations in highway runoff varied from 0.029 mg/l (McNeill and Olley, 1998) to 0.66 mg/l (Desta et al., 2007) and in thawing runoff from 1.729 mg/l (Frimmel et al., 2007) to 5.71 mg/l (Hallberg et al., 2007). Concentrations of dissolved copper (shown to be the predominant form) ranged from 0.002 mg/l (Hallberg et al., 2007) to 0.031 mg/l (Crabtree et al., 2008) and in thawing runoff from 0.023 mg/l (Hallberg et al., 2007) to 0.064 mg/l (Frimmel et al., 2007). Little information has been published on iron, although an averaged value from urban runoff established for Fe_{tot} was 3.419 mg/l and for Fe_{dis} it was 0.211 mg/l (Mosley and Peake, 2001), and this knowledge gap has been addressed in this thesis.

It has been demonstrated that runoff quality is complicated because of the variability and unpredictability in the magnitude and frequency of rainfall events. Typical factors which affect stormwater quality and, consequently, the presence and behaviour of metals have been described in previous sections and they are rainfall intensity and duration, climate, ADWP and first flush characteristics.

The “first flush” effect has been investigated by many researchers with contradictory results. Several published papers reported no strong first flush effect for contaminants, whereas other data provided evidence of a first flush of pollutants. However, much of the information reviewed was thought to be unreliable because in the majority of cases just a small number of rainfall events or even only a single one were taken into consideration rather than a series of rainfall events of different intensity.

An important factor allowing the prediction of runoff quality is ADWP. Evidence has been provided and a good theoretical case made for the assumption that the longer the ADWP, the greater will be the concentrations and loadings of pollutants. While the literature contains studies that analyse first flush characteristics and the duration of ADWP, they did not take into account rainfall intensity, which could be the main parameter for a quantitative evaluation of rainfall characteristics and soil saturation. It can be suggested on the basis of the literature review that surveying a larger number of storms would overcome the potential bias which would be caused by an over-reliance on the ADWP and the degree of soil saturation.

The literature includes data on the metal concentrations in residential and highway runoff from two principal sampling protocols, namely grab and composite sample measurements. In the case of the most common metals, Zn and Cu, most data consisted of the long-term averages obtained from composite samples. It was concluded that grab samples do not provide sufficient information to allow accurate calculation of the total pollutant load that runoff carries because of the variability in the storm cycle. Time average or flow-adjusted composite measurements enable the event mean concentration (EMC) and overall load on the catchment to be evaluated. Automatic samplers are widely used for analysing water quality parameters but they are difficult to use at remote sites with no security or power. Thus it was concluded from the literature that this research should include a detailed analysis of the rainfall characteristics to help with the analysis of ADWP. The literature review has shown that automatic composite sampling is the ideal method to use but this was beyond our resources and so field sampling included the taking of samples from a storage lagoon which could be expected to integrate some seasonal variability into the actual metal concentrations.

A wide range of metals was reported in sewage effluent and most literature on hazardous materials is concerned with their leaching from solids during treatment. Summarising the data for the same indicator metals as for highway runoff, namely, Zn, Cu, Pb and Fe, then the range can be said to have depended on the catchment type, i.e. the amount of industry concentrated in that catchment. For purely domestic sewage works the range of metals was narrower and the concentrations lower than for highway runoff. For the total zinc the range was from 0.01 mg/l (Bond, 2001) to 0.56 mg/l (Kim et al., 2002) and for dissolved copper it was similar to that for highways – from 0.009 mg/l (Bubb and Lester, 1995) to 0.02 mg/l (Matthiessen et al., 1999). This was surprising given the common use of copper for domestic water systems.

In the case of treated sewage effluent, soluble metals are representative since sewage treatment includes three solid-liquid separation stages which result in very low TSS concentrations, typically less than 5 mg/l. The review confirms that the total concentrations of metals are lower than those in highway runoff because of this effective removal of solids. Even when the much larger volumes discharged are taken into account, the effect of dilution in the receiving water and the metals' limited retention in the river systems would suggest that they have no environmental impact. The literature review therefore suggests that metal concentrations derived from highways could be greater than those from other diffuse sources in the environment. The previous work reviewed also suggests that treated sewage might still contribute significant metal loads to water bodies with low dilution. The literature does not, however, report any studies conducted with the aim of comparing reliable inputs into the same catchment. Thus an objective of this work was to evaluate differences in metal runoff concentrations, including those of iron, in individual storms of different types. The site chosen, which was adjacent to the busiest road in the East Midlands (M1), incorporated the current recommended treatment design (interceptor and SUDS). In order to compare the potential contribution of major roads with other urban sources, the discharges of the local sewage works were also measured together with three local rural streams. A second objective was to use data derived from the fieldwork to evaluate the performance of the treatment SUDS lagoons at the test site on the M1.

The previous research reviewed as well as experience gained in our own laboratory had indicated difficulties in the precise analysis of metals at these concentrations using the ISO standard methods, particularly when the metals were complexed with natural materials. Therefore, an alternative, more recently introduced microwave technique which is safer and potentially more accurate was compared with the standard method. The literature discussed has shown that particle associations and speciation affect both the toxicity and bio-availability of metals. There was also little information available on differences between soluble and total metals. It has been argued in the environmental quality standards that this is justified since soluble metals are the most bio-available. It has been hypothesised that in the case of most treatment systems, for example, interceptors, lagoons and filters, this equilibrium is not fixed, which is why another objective of this study was to analyse the factors affecting metal solubility.

Understanding the chemical properties of metals in the environment from this point of view will allow better models and predictions to be made regarding the efficiency of their removal. The findings from studies on the form in which metals may be present in stormwater have occasionally differed significantly, with the result that in the literature many of the results obtained contradict each other.
The objectives from this chapter are summarised and presented at the end of the Chapter 3, the literature review on enhancing stormwater treatment by filtration.

CHAPTER 3

LITERATURE REVIEW ON THE POTENTIAL OF FILTERS TO ENHANCE METAL REMOVAL FROM STORMWATER

3.1 INTRODUCTION

A number of different natural and artificial materials have been used as filter media for stormwater treatment. These include sand, coated sand, gravel, crushed glass, perlite, peat, leaf compost, mulch, zeolite, granular activated carbon and plastics (Moller et al., 2002; Datry et al., 2003; Liu et al., 2004; Liu et al., 2005; Baltrenas and Brannvall, 2006; Ray et al., 2006). However, there are few well controlled comparative tests that have been developed to study these different media outside the waste water treatment area (McLaughlan, 2004). Runoff generated from different types of urban surfaces, as noted in the previous section, is likely to have different physical and chemical properties which might affect the efficiency of filtration, as will be discussed further below (Clark et al., 2005). This review includes mainly filter applications related to urban runoff. The issues related to drinking water treatment (backwashing and slow filtration, for example) were deliberately omitted. Section 3.1.5, however, is devoted to an exploration of recycled crushed glass as a potential new filter medium; most reports are from studies where recycled glass was used either for drinking or waste water treatment.

3.2 FILTER MEDIA

3.2.1 Sand

The most common and traditional medium for filters is sand (Alexeev and Kurganov, 2000; Davis and McCuen, 2005). The performance of filters is a function of three factors: grain size, pore space between grains and contaminant size. Since contaminated solids accumulate in the pore space, they will eventually be clogged, which is why they normally include provision for backwashing. Sand filters have been used for stormwater treatment with a pre-treatment separating pond or basin. Table 3.1 summarises information about the specific surface area of sand and compares it with other filter materials. These pre-detention units serve to extend the maintenance time of the sand filter by removing some of the larger particles and sediments (Davis and McCuen, 2005). All filters will accumulate particulate matter and are difficult to clean but excess solid accumulation has to be avoided to prevent captured solids from being carried over the filter during heavy rains or perturbations to the filter.

Table 3.1 Specific surface area (SSA) of some media (modified from Davies and Wheatley, 2010)

Type of media	SSA, m^2/g
Glass	0.0558
Slate	0.1873
Drinking water sand	0.2261
Limestone	0.2502
Phosphorus slag	0.2803
Pumice	0.4864
Expanded clay	1.4685
Steel slag	2.3300
Furnace slag	6.6494
Activated carbon	1000

An example of data for metal removal by means of sand filters is summarised in Table 3.2. Barrett's data is based on the reduction of EMC.

The literature review has noted that iron and lead are affiliated with particulate matter and their removal is accomplished simultaneously. This can be seen in the removal of total Pb and Zn, but not of Cu which has been shown to be more soluble. However, it is difficult, unfortunately, to normalise the removal of pollutants by mass efficiency, for example, removal per kg on m^2 of sand surface, because the initial concentrations of metals were not given in the data. It could be useful to know these concentrations for comparison with other materials.

Table 3.2 Metal removal performance for sand filters (modified from Davis and McCuen, 2005)

Pollutant	Percentage removal	
	Urbonas (1999)	Barrett (2003)
TSS	80 - 94	90
Total Cu	20 - 40	50
Dissolved Cu	No data	6
Total Zn	80 - 90	80
Dissolved Zn	No data	36
Total Pb	No data	80
Dissolved Pb	No data	39

3.2.2 Hardwood mulch

Organic material should be a good adsorbent for polar materials and natural fibre, e.g. peat and heather are established in their use for odour and VOC treatment. Reed beds and grass swales have been selected for highway runoff because of their claimed adsorbent properties. Ray et al. (2006) investigated the performance of common garden mulch for the removal of metals from solution. The mulch was made up of a mixture of shredded peat, wet straw and leaves. The hardwood mulch sorbed metals from a sample of copper, cadmium, chromium, lead and zinc- spiked stormwater.

Table 3.3 summarises the results in terms of the percentages of metals sorbed as a function of their initial concentrations.

Table 3.3 Percentage removal of metals by mulch compost and their initial concentration (adapted from Ray et al., 2006)

Metal	Initial concentrations (µg/l) and removal [%]			
Copper	(992) [87]	(496) [77]	(248) [59]	(124) [0]
Cadmium	(1016) [86]	(508) [98]	(254) [100]	(127) [100]
Chromium (Cr^{6+})	(989) [68]	(495) [42]	(247) [0]	(124) [0]
Lead	(996) [92]	(498) [92]	(249) [87]	(125) [84]
Zinc	(1079) [72]	(540) [81]	(270) [73]	(135) [43]

The figures for the removal of the metals thought to be the most soluble, copper and chromium show the lowest values. This study also, unfortunately, provides neither information about the form of the metals (soluble or total), nor the concentration of TSS removal. The percentage of metals removed might have been different, had TSS been present in the synthetic stormwater. The spiked concentrations are also higher than those normally encountered in highway runoff (see Table 2.2). Further analysis of the solid content, in particular, but also of other parameters (pH and EC) would have been useful.

3.2.3 Polyurethane*

Synthetic media are more efficient for filtering dirty water than sand because they are likely to optimise surface area and voidage and so increase filtration velocity and the duration of filtration and decrease the need for backwashing. In Russia, for example, this type of medium is common for water filtration (10-15 mm with a pore size of 0.8 – 1.2 mm which is 10 times larger than that of drinking water sand; Alexeev and Kurganov, 2000). A plastic medium can achieve high porosity, for example, polyurethane is up to 95% porous. In waste water treatment sheet or rashig rings of PVC and PE are used for bio-filtration (CIWEM, 2000). These are specifically manufactured rather than being made from recycled waste and are commercially available in a range of specific surface areas (see Table 3.1). Table 3.4, for example, presents data for the treatment efficiency of polyurethane filter media for stormwater runoff depending on the filtration velocity and the height of the medium. The initial concentration of TSS was 200 mg/l.

The contaminant capacity of polyurethane was found to be much greater than that of sand, for example. Depending on the filtration conditions, solid retention varied from 40 to 200 kg of solids per m^3 of polyurethane (Alexeev and Kurganov, 2000). The initial head loss was 0.15 – 0.4 m per m depth and after 50 hours of filtration at a filtration velocity from 10 to 25 m/hr, the head loss reached values between

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* A **polyurethane** is any polymer consisting of a chain of organic units joined by urethane (carbamate) links. Polyurethane polymers are formed through step-growth polymerization by reacting a monomer containing at least two isocyanate functional groups with another monomer containing at least two hydroxyl (alcohol) groups in the presence of a catalyst. (http://en.wikipedia.org/wiki/Polyurethane)

0.3 and 0.9 meters. Typical sand water filters will have a maximum velocity of 10 m/hr and a similar head loss increase would be expected after 40 hrs but following the coagulation and removal of the larger solids.

Table 3.4 also shows that the filter performance deteriorates, as expected, with a decrease in the height of the medium and/or an increase in the filtration velocity.

Table 3.4 Treatment efficiency as % removal of solids at different filtration velocities and varying depths of the polyurethane medium (Alexeev and Kurganov, 2000)

Filtration velocity, m/hr	Duration of filter run, hrs							
	10	20	30	40	50	60	70	80
	Depth of the polyurethane medium is 1.5 m							
10	89.0	89.0	88.4	87.6	86.6	84.8	83.0	81.2
15	85.0	83.9	82.5	80.8	78.8	76.0	72.7	70.0
20	81.4	79.6	77.3	73.8	70.1	66.4	62.6	58.6
25	77.5	74.7	70.5	66.0	60.7	56.0	51.0	–
30	73.5	69.3	64.0	57.3	–	–	–	–
40	62.3	56.6	48.0	39.0	–	–	–	–
	Depth of the polyurethane medium is 1.0 m							
10	84.6	84.1	83.4	81.0	77.0	71.5	65.8	60.1
15	79.7	78.9	77.0	73.2	68.4	62.6	56.8	51.1
20	74.8	73.6	70.6	65.0	59.4	53.6	48.0	42.2
25	68.8	67.0	63.3	56.3	50.6	43.3	37.2	–
30	63.0	60.8	–	–	–	–	–	–
	Depth of the polyurethane medium is 0.5 m							
10	72.0	71.3	69.4	63.5	56.4	49.3	42.2	–
15	63.9	68.2	58.0	51.0	44.0	–	–	–
20	59.8	58.8	–	–	–	–	–	–

- no data

Unfortunately, no information was provided, however, about metal removal, although it was noted that this type of filter would remove metals with poor solubility, lead and iron, for example, in proportion to the solid removal.

3.2.4 Zeolites

Zeolites have been used in water treatment practice as an ion exchange medium since the late 1800's and they have been tested in the laboratory for their ability to remove metals (CRWR, 1995). A high level of metal removal was achieved when using this medium together with vermiculite* (Baltrenas and Branvall, 2006).

It was reported that the efficiency of metal removal from a prepared experimental solution was about 98.6% for Pb, 86.5% for Cu, 81.8% for Zn and Ni and 57.5% for Mn. This performance was obtained with a contact time of 720 minutes but the initial concentration of the metals was very high at 1 g/l compared to a maximum of about 1 mg/l to be expected in highway runoff.

Clark et al. (2005) analysed three media: zeolite, peat-sand mix and compost in parallel upflow columns. The metal removal efficiency was examined for different flow rates and influent conditions. Settled stormwater runoff from two sites of medium-density residential development in Hoover, Alabama were used for the filtration study. The filtrate was analysed for Pb, Cd, Zn, Cu, Cr, Fe, Ca and Mg and it was reported that zeolite had the lowest metal capture capability in comparison with the compost and peat-sand mix. Other factors, however, such as the pH of the effluent, headloss and clogging were less pronounced in the zeolite compared with the other two media studied. The results suggest that the solid-bound metals were the most important. Filter runs were longest in the compost. The main drawback of the compost medium was the generation of additional colour in the effluent. The peat-sand mix medium showed the most head loss potential due to clogging; although it was the best medium at removing dissolved metals.

Other studies (Allen et al., 2004; Kalmykova et al., 2008) have also demonstrated that peat incorporated into the filter material exhibits high adsorptive and cation

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* Vermiculite is a hydrated silicate mineral which expands on heating; it is used in insulation and as an agricultural medium for planting en.wiktionary.org/wiki/vermiculite

exchange capacity. It is known that peat consists of carbon, nitrogen and phosphorus with a composition ratio of 100:10:1, respectively. This provides a substrate for microbial growth (CRWR, 1995) which then augments the metal removal.

3.1.5 Crushed Glass

The analysis of particle size and routine TSS analysis uses vacuum filtration through 1.2 and 0.7 µm glass fibre filters (APHA, 2005).

During this process it was observed that these filters could produce significant variations in the results (see section 4.2.2). It was found that, in a number of cases, the metal concentrations present in non-filtered samples were lower than those of the filtered samples. These results suggested to us that glass was absorbing and then releasing metals. Recycled glass was, therefore, chosen as a filter medium. It is available as a low-cost waste material which is already used in construction and bedding materials for drainage pipes.

Glass is thought to be the oldest manufactured substance in the world. It is a common material for making food and drink containers. Figures published by the EPA suggest that the USA generates 12.5 million tonnes of glass waste every year, whilst in Canada the comparable figure is 850,000 tons (Rutledge and Gagnon, 2002) and in the UK it is estimated to be about 2 million tons (Hatton and Ockleston, 1997). Less than half of the total glass generated is collected for recycling, partly because of the poor market for recycled glass. Recycled glass is utilised as aggregate material for concrete, roadbeds and pavements. Recycled glass is also used as drainage material for backfill and landscaping, for the production of fibreglass and as a reflective material for paint. The application of crushed glass as a filter medium is relatively new and information and independent data about its feasibility is very scarce in the literature. No single paper or article has been found in the refereed journals about metal removal using a glass medium.

There are reports of studies in which recycled glass has been used as a filter medium for waste water treatment (Anon, 2006) and, as noted, solid removal could be used to anticipate the removal of iron, lead and cadmium from highway drainage (*http://www.sciencedirect.com*).

According to this study, glass compared well with traditional gravel for removing TSS and BOD, although, unfortunately, no data was provided about initial concentrations, effluent concentrations or how effective crushed glass was compared with gravel. Moreover, the article is uncorroborated.

In the US, because of its low population density, more than one quarter of homes use some type of on-site wastewater treatment system, for example, septic tanks, which use gravel or crushed stone as drainfields. The figures for the UK are unknown but annual replacement sales for septic tanks are more than 10,000. Nevertheless, there are regions in the US where gravel is expensive because of its scarcity and there is a search for alternative materials. A study of crushed glass was conducted as a material for biological treatment. Two types of medium, sand and crushed glass were tested (Anon, 2005). Table 3.5 summarises that data on the performance of both filter media:

Table 3.5 Performance of glass and sand used for biological treatment (Anon, 2005).

Source	**BOD_5, mg/l**	**TSS, mg/l**	**Oil and grease, mg/l**	**pH**
Glass medium effluent	7	4	6	6.4
Sand effluent	4	3	4	5.8

From these results there is no obvious statistical difference between the glass and a sand medium. The data set was also limited, with no information provided about the initial concentrations in wastewater or the range of data, flow rate or maintenance. Unfortunately, the size of medium was also not mentioned.

Slow sand filtration (SSF) was a possibility for improved metal removal (Nur Muhammad, 1998). In this case rapid gravity filtration was selected as the filtration stage to operate after the interceptor.

Another study was devoted to evaluating the effectiveness of crushed, recycled glass and three different types of sand media, namely Stielacoom sand, Trinidad Pit sand and Ellensdurg sand for slow filtration (CWC, 1995). These media were tested in the pilot columns. The crushed glass showed the greatest rate of headloss compared to the other sand media. It was suggested that crushed glass might also have an advantage because it might fluidize at lower backflow rates compared to sand based on the fact that glass has a lower density than sands, although no confirmation of this was provided. In conclusion it was suggested that crushed glass could be an effective filter medium for low-rate filtration of raw water. The study was devoted to the treatment of drinking water with regular backwashing and no information concerning metal removal was found in the paper, even though manganese, iron and aluminium commonly give rise to problems in drinking water treatment.

In 1998 CWC (CWC, 1998) prepared another report where recycled crushed glass and sand were evaluated for their performance in the high-rate filtration of drinking water or waste water. The glass used in this study was post-industrial plate glass scrap from window and door manufacture. The glass was processed through a series of crushers, dryers, and screens to remove contaminants and to produce a range of uniformly-sized filtration media. In conclusion, it was reported that crushed glass improved turbidity removal by 25%, needed less backwash water to clean the filter medium (approx. 20%) and weighed less (approx. 20%). These attributes could reduce both capital and running costs. The report did not provide any data on the removal of other parameters apart from turbidity. The report did not present any information about the removal of metals.

Rutledge and Gagnon (2002) also evaluated the performance of a pressure filter utilizing crushed glass as the filter medium by comparing it with sand media. It was found that particle removal by the crushed glass was not as good as that of the sand medium. Interesting data from the point of view of the aims of this research were the author’s reporting of residual PSD. Results showed that after 6 months of using the crushed glass medium, the filter effluent contained 50 – 70 particles/ml with diameters of more than 2 µm, whereas the sand filter produced 25 – 50 particles/ml with diameters of more than 2 µm. In other words, the sand captured more of the smaller 5–10 µm particles. This study, however, does not provide any information about metal removal. Although it is not stated, this would imply a larger glass media size, from basic filtration theory.

As was noted, commercial information suggests that crushed glass provides improved water treatment efficiency by allowing lower backwash rates and it is cheaper, not to mention the environmental benefits of using recycled glass and so avoiding waste. However, there are some disadvantages of using this material for filtration. For example, according to the literature from the EPA (*http://www.epa.gov/osw/nonhaz/define/pdfs/glass.pdf*) the use of recycled glass as an alternative medium is not yet well-established and there are no long-term operating data available. Another disadvantage for drinking water is that since each batch of glass filter medium is unique, the performance may not be readily reproducible for new designs and neither may it be predicted when it must be replaced. The glass may also be contaminated by its previous use, although this is not mentioned in the EPA report. One type of recycled glass has been approved by the UK Drinking Water Inspector (DWI) for use in water treatment (*http://www.dwi.gov.uk/drinking-water-products/index.htm*).

3.2 SUMMARY AND STATEMENT OF OBJECTIVES

It is known, for example, that road transport is responsible for about 30% of the pollution emissions to the atmosphere but it is not known what proportion of metals in the water catchment can be attributed to road transport (USGS, 2000).

The present and future Environmental Quality Standards, such as WFD, suggest that more information on metal sources in the environment will be necessary and in order to meet any higher standards stormwater will have to be treated before it discharges into water bodies. This process has begun and there are a number of systems in use for stormwater treatment from key point sources such as car parks, motorway services and petrol stations. These systems are mainly composed of an interceptor and/or SUDS (Highway Agency, 2006; Crabtree et al., 2006). They work by gravity separation, filtration or bio-filtration. Metals bound with TSS can be removed by gravity devices such as sediment traps, interceptors, swales, retention and detention ponds, whereas metals in the dissolved form can be more successfully removed by filtration. It has been shown that sand, the most traditional and common medium for filtration works well but requires maintenance because of its susceptibility to clogging. There is little information in the literature on the maintenance requirements of gravity and SUDS separators and therefore the cost of ownership of the treatment system. There was also little information on novel treatment systems, such as improved filter media for the removal of dissolved metals.

There was a scarcity of data drawing comparisons among different filter media in terms of metal removal. Most information on recycled glass, for example, was commercial. There were also few well controlled and independent studies on the field performance of the treatment systems.

In summary, the objectives derived from the literature (Chapters 2 and 3) were thus:

a) to identify suitable analytical methods for measuring the concentration of metals and their mobility in the environment (soluble and total speciation);
b) to analyse the concentrations of metals in the runoff and to assess a case study of the treatment SUDS lagoon at the test site on the M1;
c) to compare metal concentrations in treated sewage with the concentrations obtained from the M1 in order to identify the major source of metals in the catchment;
d) to evaluate the background metals in a control rural brook and compare the results with the concentration of metals in runoff from the highway (M1);
e) to assess the effects of seasonal variation, rainfall intensity and ADWP on the metal concentrations at sampling sites;

f) to analyse the factors affecting metal solubility in the runoff, by measuring other key physical and chemical parameters in stormwater in the three locations;

g) to evaluate the efficiency of crushed glass compared with standard pea-gravel filters for enhancing the treatment of stormwater to remove metals, and

h) on the basis of these studies (above) and metal characteristics, to suggest the most efficient combination of treatment mechanisms, that is gravity, adsorption and mechanical filtration.

CHAPTER 4

MATERIALS AND METHODS FOR ANALYSING RUNOFF QUANTITY AND QUALITY

4.1 EXPERIMENTAL SITES

The aim of the work, which was to increase the understanding of the behaviour of metals in stormwater runoff, was achieved by means of experimental work divided into two parts:

1. Analysing runoff quality from a major highway and comparing it with other sources in the same catchment area.

The study comprised analyses of runoff from the M1 motorway and its treatment by interceptor and lagoon next to this major highway (M1, junction 24), of the local sewage work effluents in the same catchment and of samples from a control, a rural local brook (Woodbrook), historically the catchment for the local water supply (Nanpantan). These analyses were conducted during dry and wet weather and in different seasons.

2. Laboratory tests on improved stormwater treatment (see Chapter 5).

These tests involved filtration and adsorption by different filter media.

The experimental plan of this part of the research was to determine the water quality of runoff from different sources in the local catchment and the effect of seasonal wet and dry weather. J24 was chosen because it is one of the busiest junctions in the East Midlands and is likely to represent a worst case and it is also near the University (further details are noted in the motorway subsection, 4.1.1). The second sampling sites were representative of sewage work effluents in the catchment. The literature review noted that sewage effluents were a major contribution of metals to the catchment (Bubb and Lester, 1995). These two sites were compared with samples taken from an unpolluted rural brook used for drinking water. Details of the location of the sampling sites and other catchment information are given in subsections 4.1.2 and 4.1.3.

Sampling resources were concentrated on the motorway runoff and rural brook because greater buffering of storms is available in sewage works. Therefore, changes in metal concentrations in the sewage effluent were expected to occur more slowly.

The locations chosen for sample collection were selected taking into consideration the distinctive features of the stream, such as water depth and the availability of engineering for access (outlets, inlets, drains). More details of these locations are given as follows:

4.1.1 M1, Junction 24

The location selected on the M1 was on the northbound carriageway (labelled junction 24A). This location is at Kegworth approximately 7 miles north of Loughborough. The general view of that area is shown in Figure 4.1, as well as the location of the lagoon.

This section of the M1 motorway is one of the busiest sections, linking as it does the major East Midlands cities, and it has one of the highest levels of traffic in the UK (peak traffic flows are 30,000 vehicles an hour). The test site is located at the junction of the M1 with the M42 and A50 link roads. The sample junction 24A was rebuilt in 1996 with the construction of the A50 link road and includes an interceptor and SUDS lagoon. During rainfall events the runoff flows along a ditch adjacent to the motorway which links up with the drainage from the A50 slipway by means of which runoff is channelled into an oil silt interceptor before entering a SUDS lagoon (Fig.4.2 a). It drains an impermeable area of around 3,000 m^2. The volume of the lagoon is 2000 m^3 and the average depth is 0.9 m.

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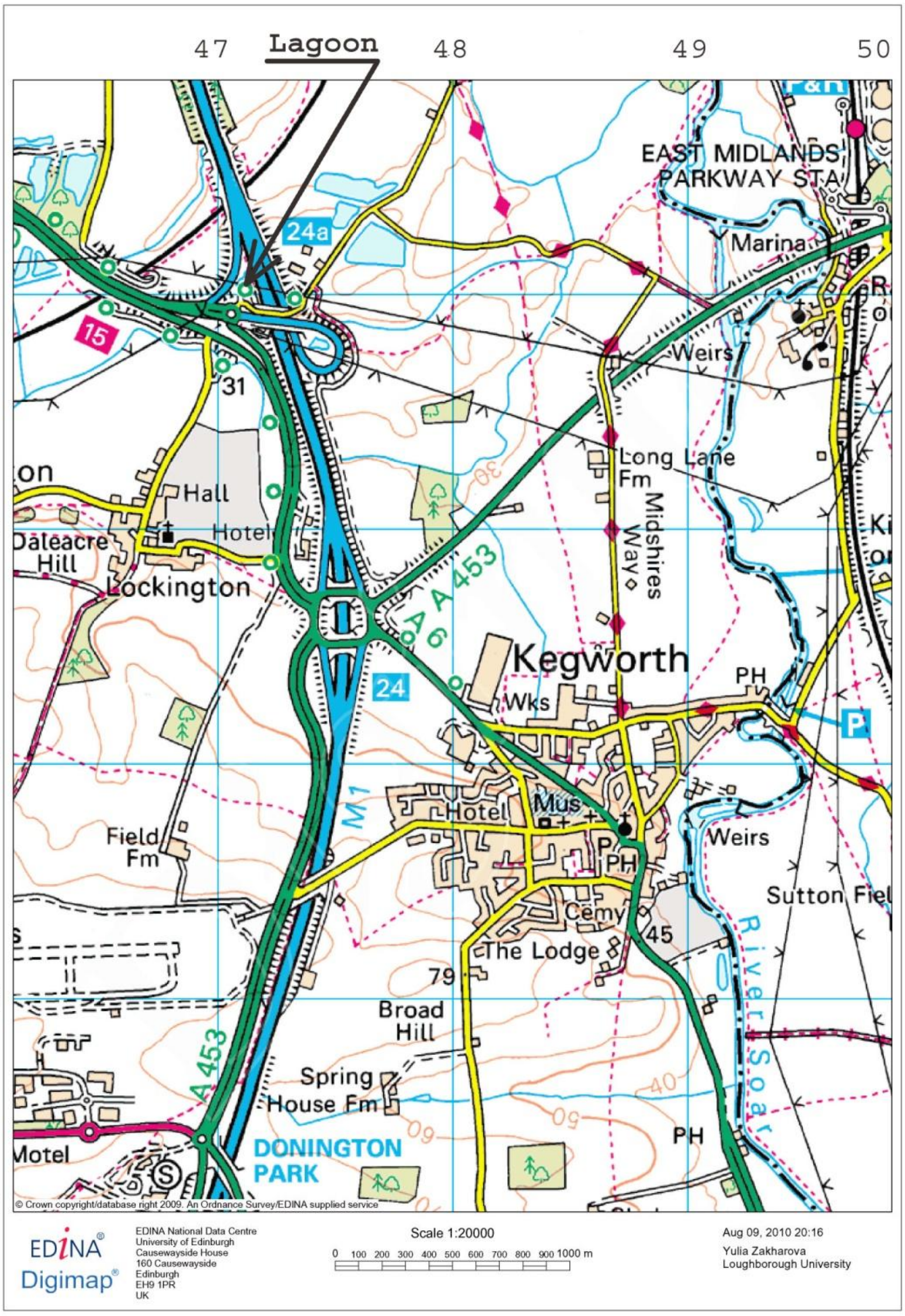


Fig. 4.1 General view of the M1 (Junction 24)

Location of sample points

Sample points were selected to observe how water quality changed through the treatment train (Fig. 4.2 b). Photos 4.1 – 4.4 show the location of each sample point.

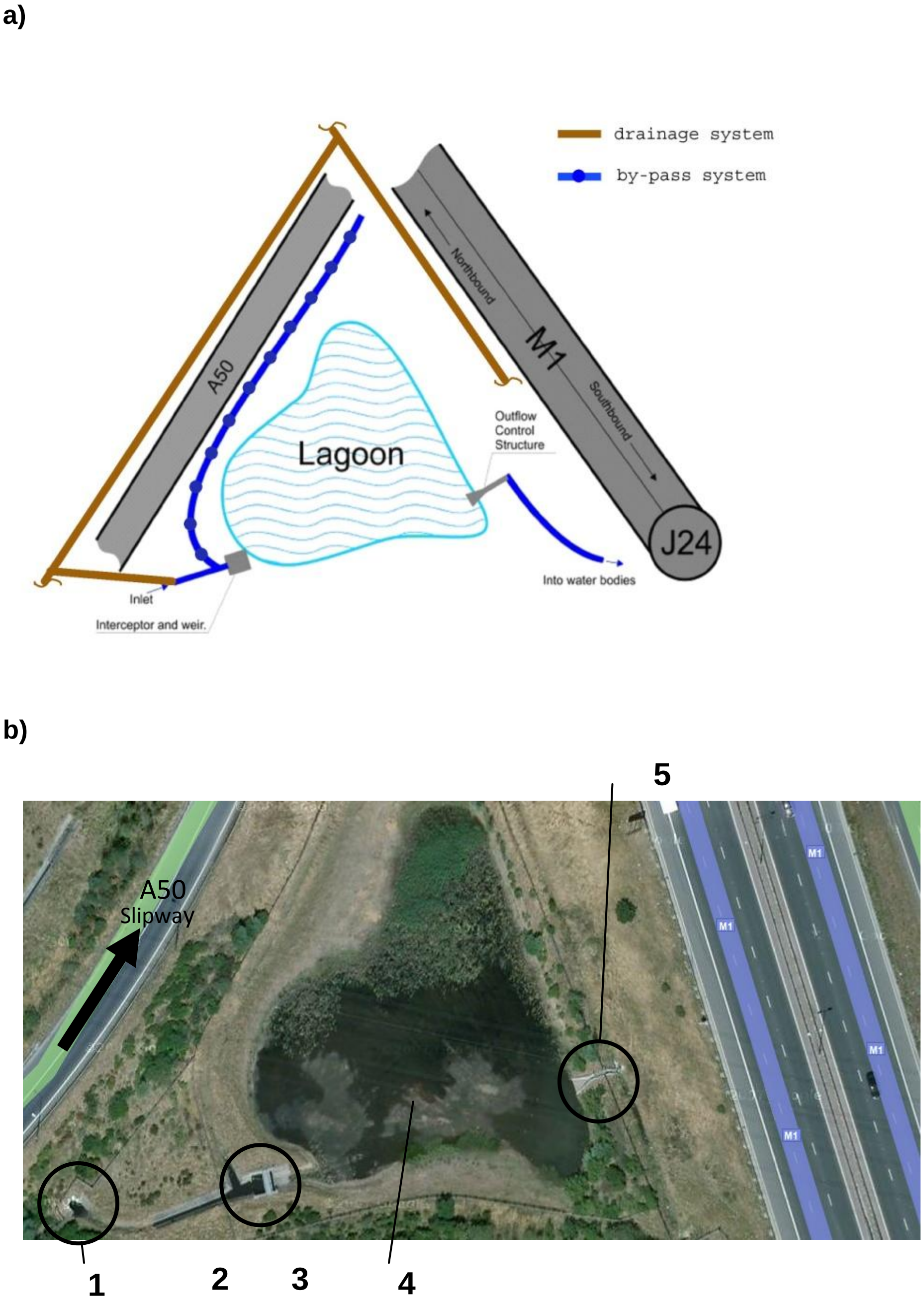


Fig. 4.2 Schematic view of the SUDS lagoon and sample points
1 – inlet; 2 – before the oil-interceptor; 3 – after the oil-interceptor; 4 – lagoon; 5 – outlet of the lagoon.

Photo 4.1 shows the inlet to the treatment system. The inlet is usually flooded except after an exceptionally dry period. Photo 4.2 shows the inlet to the separator downstream of the point shown in Photo 4.1 (about 35 m).

Photo 4.1 1st sample point. Inlet into the treatment system with the A50 above.

Photo 4.2 2nd sample point. Inlet to the oil-separator showing underflow concrete weir. Lagoon and the M1 in background

Photo 4.3 3rd sample point. Outlet from the oil-separator showing the reverse side of the concrete underflow weir shown in Photo 4.2. No flow during dry conditions.

Photo 4.4 4th sample point. The lagoon showing concrete outlet structure on far side of photograph. Sample point was taken 1/3 of the way around the perimeter of the lagoon.

Runoff comes through the perforated drainage kerbstones and surface drains of the A50 and travels through a standard concrete drain under the A50 where it mixes with runoff from the northbound M1 and enters a ditch where the first sample point is situated (Photo 4.1).The first sample point was from a shallow ditch (Photo 4.1) and during prolonged dry weather conditions (> 10 days without rain) there was either no water in the ditch or the water was completely stagnant, having been retained from previous rainfalls. Throughout the monitoring period covered by this thesis it was noted that this retained water, even though stagnant, was always turbid. This was assumed to be due to the small particle sizes and there was a suggestion that particles from the sediment might be re-suspended as a result of activity in the ditch. During rainfall events the stormwater from both the

A50 and the M1 mixes with any stagnant water present and then passes into the oil-separator (2nd sample point). Table 4.1 shows the dimensions of the oil-separator and Fig. 4.3 represents the oil-separator diagrammatically.

Table 4.1 Dimensions of the oil-separator

Length, m	Width, m	Operating depth, m
3.0	3.5	0.7

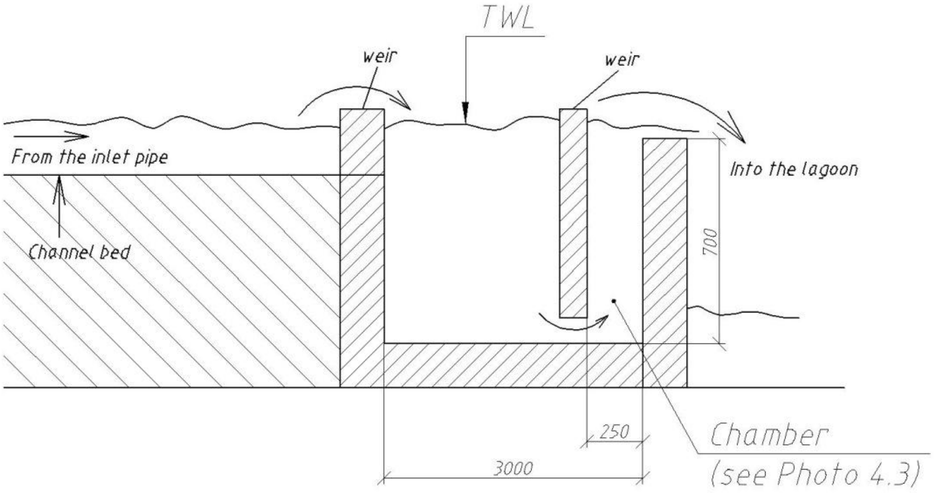


Fig. 4.3 Diagram of the oil-separator

Subsequently, following the underflow weir in the interceptor, the stormwater passes into the lagoon itself (3rd sample point). Samples were taken from the same locations in the lagoon as close to the outlet as safety permitted. Other samples were periodically taken from the lagoon in order to understand how water quality could vary depending on the retention time in the lagoon (4th sample point). The lagoon is large (2000 m^2) and it was anticipated that water quality in the outlet area of the lagoon would not vary to a great extent during dry and normal or average stormy wet weather. In the beginning of the experimental work the discharge from the lagoon was also sampled at the inlet (sample point 5, Fig. 4.2 b) to confirm this. However, it was abandoned later on since the water quality at that point was not different from that at sample point 4 (Fig. 4.2 b and Photo 4.4).

The size of the lagoon, which serves about 3000 m^2 of impervious area according to the construction drawings (Scott Wilson), was a surprise (annual average rainfall is ~ 50 mm/month; see Appendix 1 for details). It is suggested from this data that the design was based on the area available rather than anticipated volumes. It may have been intended to connect with more of the northbound surface drainage in the future. Another explanation for having such a big area of lagoon could be the conservation of wildlife and it could also be attributed to climate change issues.

Photo 4.5 shows the outflow control structure (hydraulic brake) which controls the water level in the system. When the lagoon is completely flooded, the water flows through the drain pipe illustrated and enters another ditch running along the M1 (Photo 4.6) from where it discharges into a natural water course.

Photo 4.5 Outflow control structure

Photo 4.6 Ditch running alongside the M1

Flow Rate Measurement

To measure the discharge from the motorway catchment into the inlet a “STARFLOW” Ultrasonic Doppler Instrument (*Starflow Model 6526B*) was used (Photo 4.7). The instrument measures water velocity, depth and temperature integrated into a single unit. Water velocity is measured acoustically by recording the Doppler shift from particles and air bubbles carried in the water. Water depth is measured by a pressure transducer which records the hydrostatic pressure of the water above the instrument. Temperature is measured in order to refine the acoustic recordings, which are affected by the temperature. The STARFLOW was installed in the inlet pipe with a diameter of 1000 mm (Photo 4.7) near the downstream end so as to maximise non-turbulent flow conditions and it was positioned with the sensor pointing upstream.

Photo 4.7 Flow meter in the inlet during dry weather period

Photo 4.7 shows the flow meter during a dry weather period when no water was in the inlet. Table 4.2 summarises some important characteristics of the flow meter.

Measuring Water Velocity

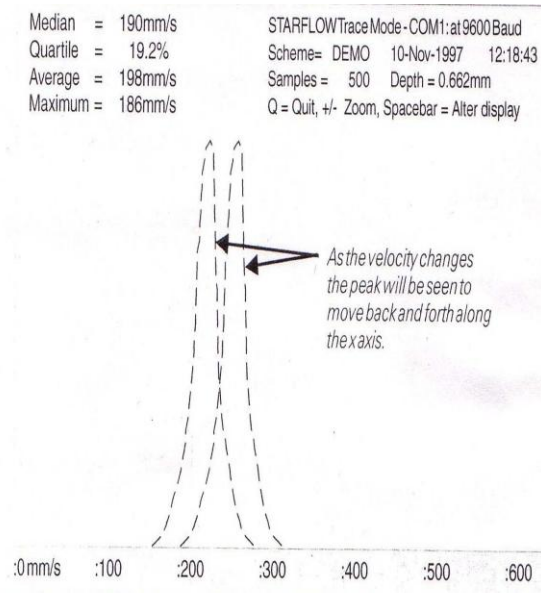
This was carried out by measuring the cross section of the inlet pipe and the average velocity during a certain period of time. Starflow measures velocity with the use of the Doppler shift which occurs when sound is reflected from a moving target; its frequency then varies according to the velocity of that target. The flow meter let out a continuous signal (incoherent) and the mean velocity of all passing particles was calculated to gain the most accurate data possible.

Table 4.2 Specifications, factory settings and performance of the flow meter

Size, (LxBxH), mm	290x70x25
Velocity, mm/sec:	
accuracy	2% of measured velocity
signal path	30° above horizontal
range	21mm/s to 4500mm/s bidirectional
resolution	1 mm/s
Depth, mm:	
accuracy	+/- 0.25% of calibrated lower range
minimum depth	25 mm
type	Hydrostatic pressure sensor
Temperature Range	-17°C to 60°C
Scan Rate, sec	Frequency of STARFLOW measurement cycle, 60 sec
Log Interval, min	Frequency of STARFLOW recordings 15 minutes
Maximum Sampling Duration	10 seconds (factory settings 2 sec)
Maximum Samples	200
Quartile	300% (factory settings 100)
Cross-sectional area	Calculated by STARFLOW using the measured depth, m^2
Flow rate, l/s	Instantaneous flow rate, calculated by STARFLOW as the product of Velocity and Area

Fig. 4.4 shows one of the velocity histograms which could be seen on the laptop screen when the STARFLOW was operating. This diagram represents the STARFLOW's view of the inlet pipe. Normally, the screen will cycle continuously, refreshing the plot and summaries each time a new set of data is acquired. The statistical parameters are continuously averaged and an example is tabulated below in Fig. 4.4.

From Fig. 4.4 one can see that the *x* axis represents the velocity in mm/s. The *y* axis indicates the relative number of times a particular velocity has been received. The centre of this peak is the mean of all echoes received. As the velocity changes, the peak will be seen to move back and forth along the *x* axis. The width of the peak indicates the range of particle velocities that are being measured with each reading. The narrower the peaks in Fig. 4.4, the lower the standard deviation, and in practice, the closer to laminar (mean velocities from 50 to 100 mm/s). In fast turbulent water the peak can be 500 mm/s or more wide because of the range of velocities present in eddies and swirls.



Median = 190mm/s
Quartile = 19.2%
Average = 198mm/s
Maximum = 186mm/s

STARFLOWTraceMode-COM1:at9600Baud
Scheme= DEMO 10-Nov-1997 12:18:43
Samples = 500 Depth = 0.662mm
Q = Quit, +/- Zoom, Spacebar = Alter display

As the velocity changes the peak will be seen to move back and forth along the x axis.

Median, mm/s	*The computed median of all the Doppler shifts detected.*
Quartile, %	*A ratio of the width of the peak to the height. This provides an indication of the quality of the histogram. Normal values are from 20% to 50%. If the transducer is buried in silt, the values will be from 100% to 200% (factory settings).*
Average, mm/s	*The mathematical average of all measured velocities. This can be unacceptably biased by signal noise.*
Maximum, mm/s	*The Doppler shift of the peak of the histogram.*

Fig. 4.4 Velocity histograms of the operating flow meter

From the data presented in Appendix 3, one can see that in most cases the flow regime was uniform with the velocity ranging from 20 to 60 mm/s. When the velocity was less than 20 mm/s, the flow rate data were not taken into consideration.

The site was visited at least weekly to ensure that the flow meter had not been disrupted and was safe and these inspections were carried out at the same time as sampling. Data for flow rates during the week were downloaded during these visits. Photo 4.8 shows the laptop linked to the logger. The flow meter was re-programmed before leaving the site.

The Starflow cable contained a tube to vent the depth pressure sensor to air. Inspections of this tube were necessary at each visit to ensure that no moisture or insects entered the vent tube, as this would have caused erratic depth measurements.

Photo 4.8 The laptop connected to the logger

Depth Measurement

Water pressure was ascertained via a pressure manifold. The manifold's shape helped reduce the effects of velocity on the pressure sensor so that a more accurate measurement could be taken in relation to depth.

Factors Affecting Data Accuracy

The accuracy of the measured velocity depended on the flow and cross-sectional characteristics of the site. Smooth and uniform is desired, which was mostly the case at the test site, along with a constant cross-section, which the pipe at the site provided.

One of the factors which affects the data from the flow meter is variations arising in the velocity distribution across the channel when averaged velocity is used as opposed to instantaneous measurement. This occurs when particles (on velocity streams) wander from side to side as they move along the channel, which can cause 10% differences from some of the averaged particle velocities. There is nothing which can be done about this and it is part of the overall error that occurs when analysing data from this type of flow meter.

Another influence on accuracy is the conversion of the logged velocity data into a mean velocity. The larger the channel, the smaller the number of representative particles the Starflow will measure. As the outlet pipe is not large, this factor should not have had a significant effect on flow.

Flow Meter Problems

Initially the field work encountered unexpected difficulties because of the poor reproducibility experienced from the unit. The unit was found to be sensitive to debris and silt deposits on the sensors, as well as the nocturnal activities of animals. This was recognised from the erratic data produced (see Appendix 3). To improve the situation, some settings were changed to reduce the range of values included for better interpretation of the data. Table 4.3 shows both the default settings set by the software and those which were changed.

Table 4.3 Factory settings and later adjustments

Settings	Factory settings	Changed to
Max Quartile settings, %	100	300
Min samples to analyse	20	10
Max sampling time	2	10

As was mentioned above, a Max Quartile value equal to 100% indicates that the unit was buried under the silt (Fig. 4.4), which could not have been avoided, especially after a prolonged spell of dry weather. Hence, the setting of the quartile reading was changed from 100 to 300, thereby spreading the Doppler shifts wider and resulting in a better performance, as the unit was forced to perform in more severe and unfavourable conditions. The changes in the quartile settings meant that the frequency of sampling needed to be adjusted (Table 4.3). It has to be noted that all these changes affected the accuracy of the data, since the number of particles counted was reduced by half.

4.1.2 Woodbrook

This brook rises in the Charnwood hills to the South West of Loughborough (see Fig. 4.5). The brook flows through the centre of Loughborough to join the river

Soar. Woodbrook was originally impounded upstream of Loughborough (1895) to supply drinking water for the town (but it is now redundant in this function).

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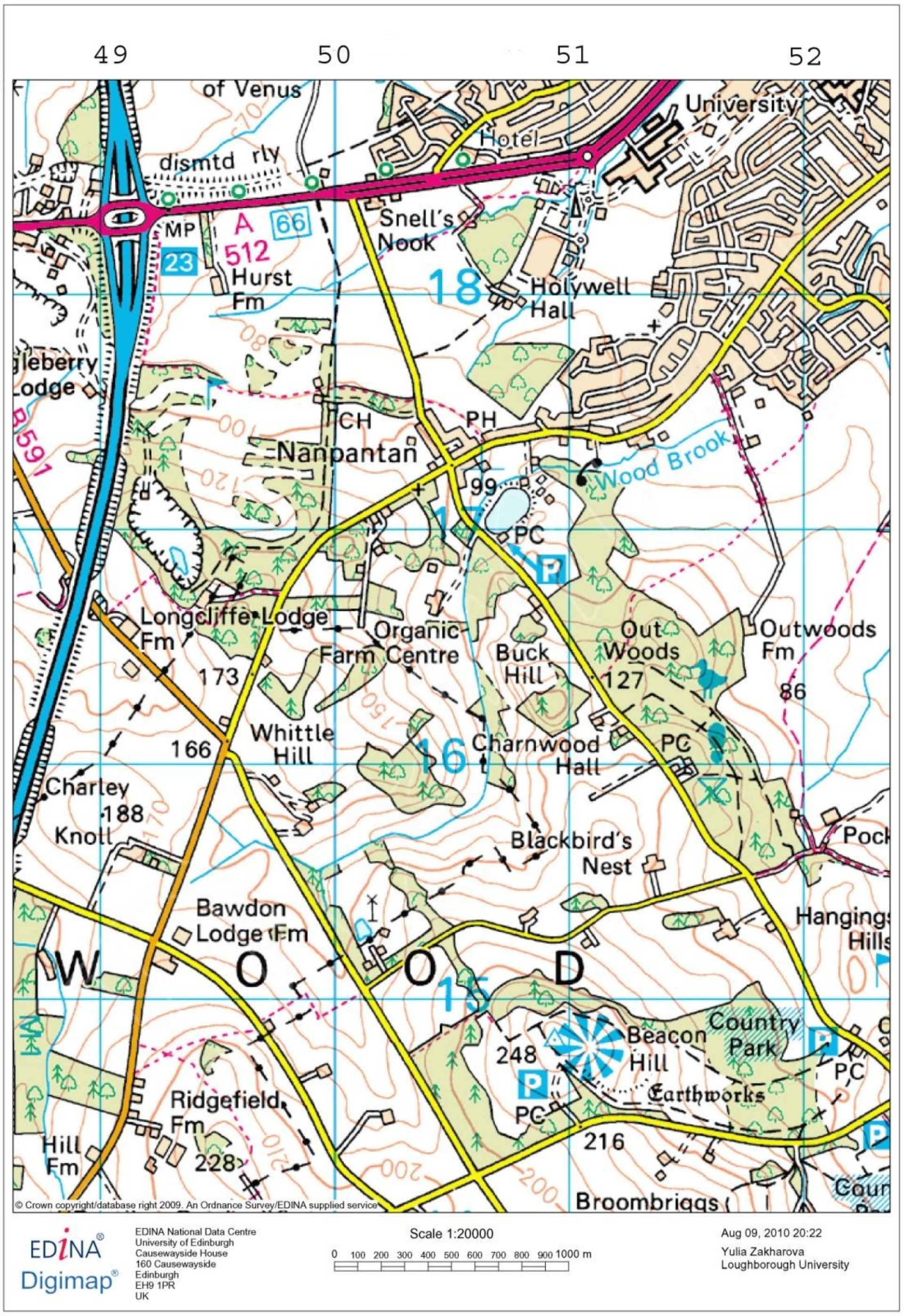


Fig. 4.5 The location map shows the source catchment upstream of the sampling point of Woodbrook, its proximity to the M1 and the University

It is an overflow stream from the water works reservoir and it has an average flow rate during dry weather flow of 50 l/s in Loughborough. The area upstream of the sampling point flows through agricultural land, family gardens, allotments adjacent to houses, minor residential roads and their grass verges (see Fig. 4.5). The area enclosed by the catchment boundary is approximately 25.5 km^2. The sampling site can be seen in Fig. 4.6 and Photo 4.9.

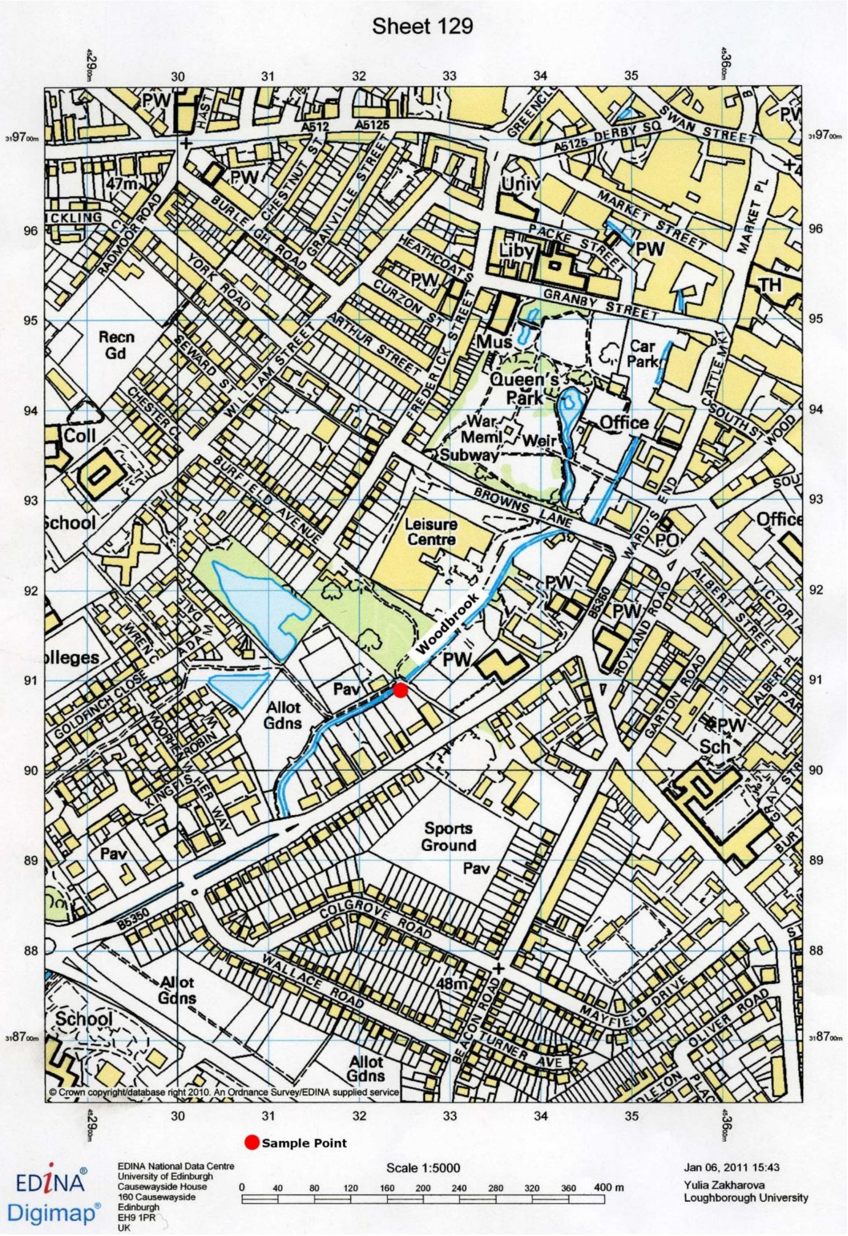


Fig. 4.6 Woodbrook sample point

Photo 4.9 Woodbrook sample point

The main criterion for choosing a sampling location was safety of access and finding a place in the brook where samples could be assumed to be representative of the average quality of brook particulates. The place was chosen while taking into consideration erosion, transportation and deposition of sediment. An area of the bed of the brook was chosen with a substantial proportion of silt but so as to be free from coarse material (pebbles and gravel), except under extreme weather conditions. Sampling was not carried out during very low-flow periods and, consequently, always included TSS, inputs from silt and land erosion. In order to investigate the effects of season on residential runoff on the quality of the otherwise rural Woodbrook, sampling was differentiated according to rainy and dry periods. Pollutants were classified as derived either from soil (N and P) or urban sources (EC & metals).

4.1.3 Sewage treatment works

Table 4.4 summarises information about STW flow and sources of pollutants.

Table 4.4 STW (type of treatment)

Name of STW	Type of treatment
Loughborough	Standard A/S
Osgathorpe (Coalville)	Filters
Shepshed	Oxidation ditch
Leicester	Standard A/S

The location area of the STW is represented by Fig. 4.7 and the sampling site of the Osgathorpe STW (final effluent) (SW1) can be seen in Photo 4.10.

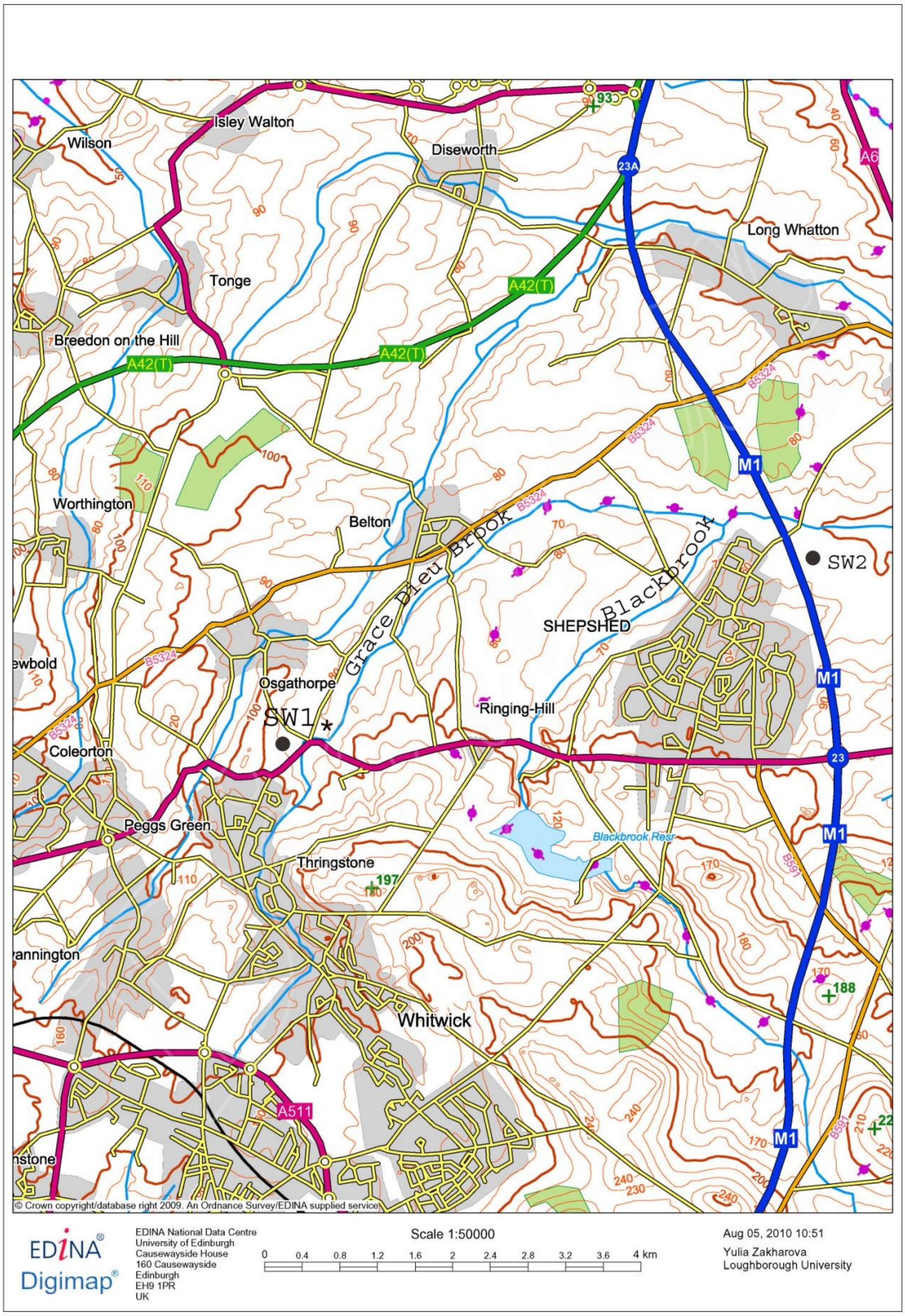


Fig. 4.7 Location area of the sewage works sampling sites. SW1 – Osgathorpe sewage works and * - sampling point of the final effluent; SW2 – Shepshed sewage works.

Photo 4.10 Final effluent of the Osgathorpe sewage works

Only the final effluent was sampled and thus it might be expected that any insoluble pollutants would have been removed by the settlement stages of sewage treatment.

4.2 SAMPLE COLLECTION AND PREPARATION FOR ANALYSIS

4.2.1 Sampling Procedure

Treatment lagoon

Samples were collected both during dry and wet weather from the M1 treatment lagoon and in different seasons. During dry weather, single grab samples were collected and the water depth at the sampling points was recorded. To observe dynamic fluctuations of the pollutant concentrations during wet weather, a number of grab samples were taken during storms, depending on the rainfall characteristics, to take into account the variability.

The amount of rainfall was recorded by a rain gauge which was used only during sample collection and linked to the volume of runoff and frequencies of sample collection. The area for rain gauge installation was selected to be free from trees, bushes and long grass. The rain gauge was set up on the moss surface adjacent to the interceptor.

In the course of the study a portable flow meter was purchased which enabled measurements to be taken of the flow rate and, consequently, of mass pollutants over a rainfall event.

Rural brook

Grab samples were also collected both during dry and wet weather and in different seasons from a local brook (Fig 4.6). Two attempts were made to install a rain gauge in the vicinity of the brook sample point, both of which ended up with the loss of the rain gauges: one of them was probably stolen and the other was blown or washed away.

Sewage treatment works

It was reasoned that there was buffering in the sewage system and samples of the STW effluent were therefore collected according to resources rather than specific weather conditions.

Limitations

The two limitations that were encountered during the research which required change were problems relating to the monitoring or measuring of the flow rate (the flow monitoring problems are described in section 4.1.1); and the need to improve the analytical technique on the basis of experience gained. After March 2008 the microwave digestion technique was used exclusively and the details are shown in Table 4.5

4.2.2 Sample preparation

Samples were collected by hand using pre-washed polyethylene bottles which were kept stored and soaked in a 50% solution of HNO_3. Before sample collection,

Table 4.5 Samples affected by the change in analytical technique

Term of sampling	M1 (J24)	Woodbrook	Sewage Treatment Works			
			Loughborough	Osgathorpe	Shepshed	Leicester
Oct. 2006	■	■				
Nov. 2006	■	■				
Dec. 2006	■	■				
Jan. 2007	■	■				
Feb. 2007	■	■				
March 2007	■	■				
Apr. 2007	■	■				
May 2007	■	■				
June 2007	■	■				
July 2007	■	■				
Aug. 2007						
Sept. 2007	■	■				
Oct. 2007	■	■				
Nov.2007			■	■	■	■
Dec. 2007	■	■	■	■	■	
Jan. 2008	■	■	■	■		■
Feb. 2008						
March 2008			●			
Apr. 2008	●	●				
May 2008	●	●	●			
June 2008	●	●				
July 2008	●	●	●			
Aug. 2008						
Sept. 2008	●	●				
Oct. 2008			●			
Nov.2008	●	●				
Dec. 2008	●	●				
Jan. 2009	●	●	●			
Feb. 2009		●				
March 2009	●	●	●			
Apr. 2009	●	●	●			
May 2009	●	●	●			
June 2009			●			
July 2009	●	●	●			
Aug. 2009	●	●	●			
Sept. 2009	●	●	●			
Oct. 2009	●	●	●			
Nov.2009	●	●	●			

■– Hot plate; ● – Microwave digestion; March 2008 – a microwave digester was purchased

the bottle was rinsed twice with the sample. Subsamples for the analysis of metals (100ml aliquots) were acidified as soon as possible on return to the laboratory with concentrated HNO_3 (5 ml/l). For the analysis of dissolved metals, a similar 100ml of sample was filtered under vacuum through a 0.45 μm pre-acid-washed membrane filter and stored in an acid-washed plastic bottle. Photo 4.11 shows the standard commercial filtration unit for a 0.45 µm membrane filter. The filtered samples were also acidified with concentrated HNO_3 to pH < 2.

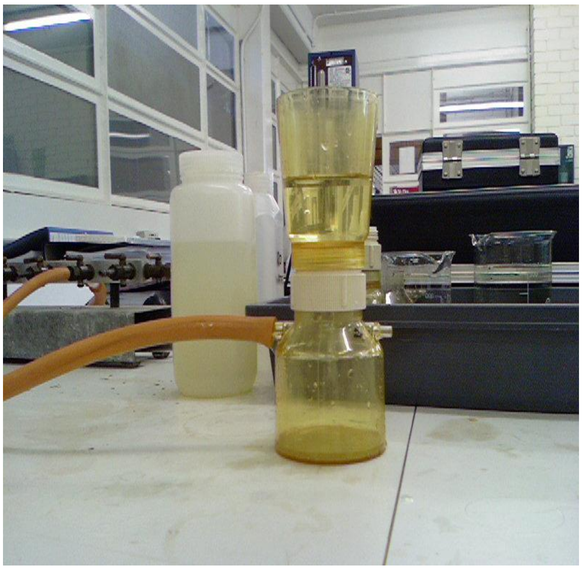


Photo 4.11 Filtration unit 0.45 µm membrane filter

To analyse the behaviour of metals (affiliation with different particle sizes) samples were also filtered through 1.2 and 0.7 µm pore-size filters made of glass fibre paper (this allows the proportion of attachment to organic solids of different sizes to be analysed).

Samples for analysing NO_3^- were collected in other plastic bottles without soaking in the solution of NO_3^-.

Samples for other analyses (see section 4.2.4) were stored at 4°C until the analyses could be performed, usually within 24 hours.

Total metal analysis with hot plates

Total metals were analysed by means of two digestion techniques: the APHA 2005, Standard method and the Aqua Regia method. According to the APHA, digestion is carried out in three stages. For stage 1, 100 ml of sample was transferred to a flask, acidified with concentrated HNO_3 (3 ml) and heated on a hot plate to evaporate and reduce the volume to less than 5 ml. At the second stage the sample was acidified with a further 5 ml of HNO_3 and heated until digestion was complete (a standard indicator of completion of digestion was a light-coloured solid-free sample). For the third stage it is necessary to dissolve any remaining precipitate or residue which might be left after the previous stages. For this purpose, 10 ml of 50% dilution of concentrated HCl and 15 ml of metal-free RO water were added and heated for an additional 15 minutes. The samples were then cooled and filtered (Whatman no. 1) to remove insoluble material that could have clogged ICP's nebuliser.

The Aqua Regia method is a less rigorous procedure but it is quicker as it is carried out in one stage. 100 ml of sample was acidified with 2 ml of concentrated HNO_3 and 5 ml of concentrated HCl and then heated on a hot plate until the volume was reduced to approximately 25 ml.

In both cases (Standard methods and Aqua Regia) it is undesirable to boil the samples because at high temperatures metals tend to break their bonds with particulate matter and boiling is likely to be a cause of the formation of new bonds and complexes. Moreover, some more volatile metals might be evaporated off, so the temperature during evaporation should be 90 - 95˚C (APHA 2005).

Total metal analysis with microwave digestion

During the course of the study a microwave digester was purchased which enabled the third method of total metal recovery to be implemented. Microwave digestion was performed in a commercial CEM *Mars Xpress* microwave, using 30 ml of sample which was acidified with 2 ml of concentrated HNO_3 and 5 ml of concentrated HCl. When the samples were cooled, they were filtered through Whatman no.1 and diluted with distilled deionised water to 50 ml in volumetric flasks.

Total and dissolved metals were then tested from all samples using an Inductively Coupled Plasma (ICP) analyser *(Thermo Jarrel Ash Atom Scan 16*). The ICP's detection limit for each of the tested elements is dependent on its wavelength and is presented in Table 4.6.

Table 4.6 ICP's detection limit

Element	**Wavelength, nm**	**Detection limit, mg/l**	**Element**	**Wavelength, nm**	**Detection limit, mg/l**
Fe	259.940	0.002	Ni	221.647	0.005
Cr	283.563	0.004	Pb	220.353	0.025
Cu	324.754	0.002	Zn	213.856	0.002

4.2.3 Particle size distribution (PSD)

This analysis was carried out with samples from the M1 collected during wet weather to evaluate the settlement characteristics and performance of the lagoon. Samples for PSD were also taken before passing through the oil-separator and after it. Analysis was carried out by means of a “Mastersizer” 2000 analyser (Malvern Instruments) which allows particles to be measured in a range from 0.02 µm to 2000 µm with a degree of reproducibility that depends on the obscuration factor, i.e. the particle concentration from 10 to 20%.

In the course of the study PSD was also carried out for the second part of the experimental programme (column experiment), i.e. while determining the efficiency of the filter materials. In this case samples were taken from the feed to the column and the effluents were sampled at various stages of filtration. The analysis had to be carried out using the Mastersizer below its recommended obscuration level, which could have resulted in an error in the final effluent values. This type of analysis was easier to reproduce than the alternative image analysis. The water after filtration (column experiment) had a TSS concentration of up to 10 mg/l.

4.2.4 Other physico-chemical analysis

These were all carried out in accordance with international standard methods (APHA 2005).

pH, TDS and Electro conductivity. These parameters were measured by using a pH-EC-TDS meter *Hanna HI 9812*. The detection range of the equipment for TDS and EC measurements was 0 to 2000 in ppm or µS/cm but during winter, because of the presence of de-icer salts, the samples needed to be diluted.

The pH meter was buffered before use and the EC/TDS required calibration only 1 – 2 times a year according to the manufacturer.

Total Suspended Solids (TSS) were determined by filtration of a water sample using a 1.2 µm grade GFC, 7 cm discs. The discs were weighed before and after filtration and the results were expressed so as to give the suspended solid concentration in mg/l. The volume of water to be used for filtration was determined by visual inspection of the solid load (see Table 4.7).

Table 4.7 Volume of water samples for TSS determination from sampling sites

Name of sample	Volume of sample, ml
Sewage treatment works	250 – 300
Woodbrook (dry weather)	
M1 (J24) (dry weather)	100
M1 (J24) (wet weather)	50 – 100
Woodbrook (wet weather)	

Samples were dried in an oven at 105ºC for 1 hr, cooled in a desiccator and reweighed after a second hour to ensure constant weight.

Total organic carbon (TOC) was determined by the high-temperature combustion method using a Total Organic Carbon analyser *Rosemount Dohrmman DC 190*. The samples were settled but not filtered prior to the analysis.

The analyses of Nitrate and Phosphate were carried out by means of the ion-chromatographic method *Dionex ICS – 1000*, using 10 ml of samples which were occasionally filtered to avoid clogging the column.

Total hardness was determined utilising a commercial test kit tablet test with *Palintest Photometer 5000.*

CHAPTER 5

EXPERIMENTAL SET-UP FOR FILTRATION AND ADSORPTION STUDY

5.1 THE DESIGN OF THE FILTER UNIT AND ITS DESCRIPTION

It has been shown in the literature review that the quantity and type of metals and other water parameters of highway runoff can vary widely depending on the sampling point, as well as both within and between storm events (Crabtree et al., 2006; Prestes et al., 2006). Moreover, from the literature review it can be seen that the amount of suspended solids in highway runoff is significant and influential on the total metal concentration. This is recognised and particularly important for Zn since the EQS is expressed as a total. Following the literature survey and previous work at Loughborough (Nur Muhammad, 1998), it was uncertain how well the recommended highway runoff treatments (interceptor and SUDS) would perform in achieving the EQS under all conditions. Thus, a series of experiments were carried out to explore the effects of augmenting separator performance with a filter as recommended in PPS 25 and the CIRIA guide (2000).The opportunity was also taken to evaluate the efficiency of recycled crushed glass as a sustainable substitute for gravel.

This work may also be useful to guide the maintenance of filter drains which are known to collect a substantial portion of solids together with metals. According to Rowlands (2007), the road network in England is around 7,500 km in length and filter drains cover around 50% of the network and could be making an important contribution to water quality. Santhalingham (2008) of the Highways Agency highlighted the fact that the provision of effective maintenance of sub-surface drainage was a major part of their strategy to minimise the impact on the aquatic environment.

The experiment was performed in standard laboratory-scale adsorption columns made of perspex. The height of the column was 2.0 metres with an internal diameter of 150 mm. In order to assess the performance of crushed recycled glass, an identical column filled with standard highway drainage pea-gravel was used as a control (see Photo 5.1). There were two layers of media: a layer of crushed glass or pea-gravel (6 – 10 mm) supported on a layer of larger gravel (10 – 12 mm).

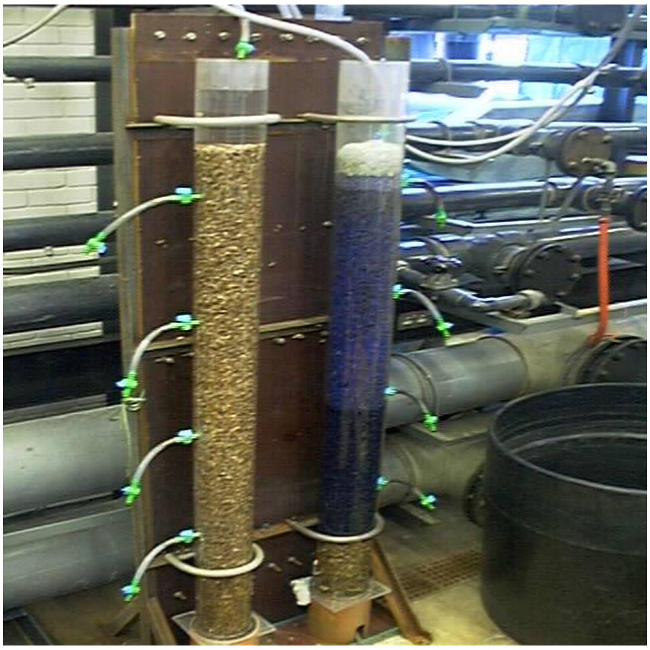


Photo 5.1 Photograph of the two units

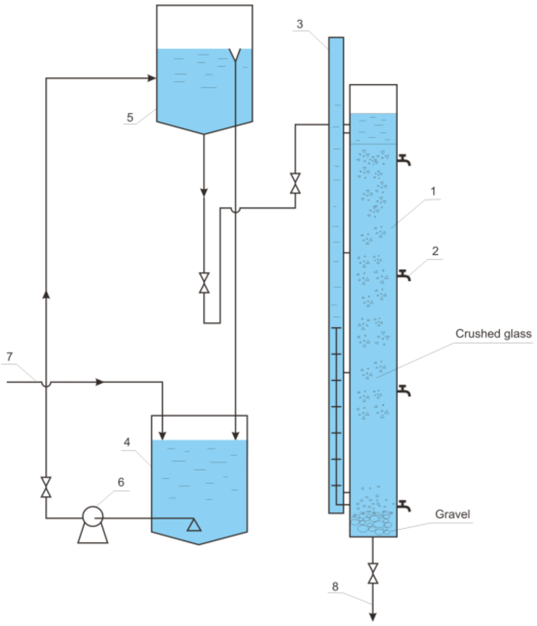


Fig. 5.1 Schematic diagram of the column 1 - filter filled with crushed glass and pea-gravel; 2-sample point; 3 – piezometer; 4 – tank for supplying filter with water; 5 – tank to provide constant level; 6–pump; 7 – raw water for filtration; 8 – final effluent.

Filtered water was discharged through the base of the column. Along the column height there were also several intermediate sample points so as to evaluate the breakthrough curve (Photo 5.1 and Fig. 5.1). The first outlet is 45 cm from the bottom of the column and the rest are spaced 40 cm from each other for its full height. The filter was of a standard gravity design and it utilised a downflow velocity of between 3 and 10 m/hr to enable a comparison to be made with previous work on drinking water treatment units. Experience showed that reproducing the exact concentration of suspended solids was impossible. This was attributed to the real and variable nature of the sediment taken from the M1 and the lagoon and solid accumulation in the apparatus. In the event this simulated the likely variability in storm flows from a highway which would not be at a steady velocity or encounter a clean filter bed.

There would be changes in filtration velocity, even under the same storm conditions, caused by a combination of factors: variation in the ditch cross-section, bed gradient and the presence of the interceptor.
For metal analysis the microwave technique described in section 4.4.2 was used.

Based on experience gained when using GF filter papers (section 4.2.2), it was assumed that on delivery the crushed glass would initially be contaminated with metals. Accordingly, the medium was washed and soaked using a 10% dilution of concentrated HNO_3 until the concentrations of leached metal were negligible. The medium was tested for metals before and after being soaked. Table 5.1 compares the results of glass testing before and after soaking. Next the crushed glass was put into the column and the medium was then washed further until negligible measurements of metal concentrations were achieved (Table 5.2).

Table 5.1 Comparison of recycled glass for the presence of total metals before and after being soaked

	Fe, ppm	**Cu, ppm**	**Zn, ppm**	**Pb, ppm**	**Cr, ppm**	**Ni, ppm**	**Mo, ppm**	**Cd, ppm**
Glass before soaking	5.967	0.414	0.111	0.030	0.081	0.047	0.006	0.007
Glass after soaking	0.162	0.032	0.016	No data	Less than detected limit of the ICP	0.022	No data	No data

Table 5.2 Recycled glass in the column. (Column was filled with tap water. Digested samples)

Name of the sample	**Fe, ppm**	**Cu, ppm**	**Zn, ppm**
Tap1	0.015	0.005	0.008
Tap 2	0.019	0.007	0.008
Tap 3	0.020	0.008	0.009
Tap 4	0.022	0.01	0.009

5.2 FILTRATION AND SAMPLE COLLECTION

An experimental stock solution of 450 l was prepared with approximately 100 mg/l of TSS made up by re-suspending the sediment collected from the inlet of the lagoon at the field station on the M1 (see Fig. 4.2 b). Water was supplied to the top of the filter by a centrifugal pump (Fig. 5.1). The filter rate was 5 m/hr, which is typical of a gravity filter (Hendricks, 2006). Grab samples were collected from each sample point every hour using pre-washed 400 ml polyethylene beakers. Sub-samples for the analysis of metals (100 ml aliquots) were immediately acidified with concentrated HNO_3 (5 ml/l), as noted. For the analysis of metals the method was that which is described in section 4.2.2.

5.3 SURFACE AREA MEASUREMENT

The measurement used is commonly employed, although it has not been confirmed as an international standard (Cerato and Lutenegger, 2002). The technique uses weight gain from ethylene glycol adsorption to assess surface area. The analysis was carried out in duplicate. Aluminium sample dishes are pre-weighed (m_1) and then filled with the filter media as a blank (m_2) before being dried in a desiccator containing phosphorus pentoxide as a desiccant (70 grams of anhydrous phosphorus pentoxide). The aluminium dishes with their contents were arranged around the circumference of the desiccator and, after the desiccator had been evacuated for 45 minutes, they were then allowed to stand for 4 hours. The pump air-inlet was then opened slowly to gradually release the vacuum. The initial dry mass of the dishes was then recorded as m_3 and the dishes were returned to the desiccator immediately. It was then evacuated again for another 45 minutes before being allowed to stand overnight under vacuum. Then, on the following day, the vacuum was released gradually, the dishes were immediately re-weighed and the lowest recorded value of m_3 was noted. Sufficient volumes of ethylene glycol were then added to each dish to submerge the surfaces of the filter media and the anhydrous phosphorus pentoxide was replaced with anhydrous calcium chloride. The desiccator lid was replaced and the dessicator was allowed to equilibrate for 2 hours. The pump was then switched on for 15 minutes with the air-ballast setting of the pump open to remove the non-adsorbed ethylene glycol and subsequently the desiccator was left for 45 minutes with the air-ballast setting switched off, on the assumption that by then no residual ethylene glycol would remain. The whole system was then allowed to stand overnight under vacuum. The following morning, the vacuum was released gradually and the dishes weighed immediately, with the weights recorded as m_4.

The surface areas of the samples were then calculated from the following equation:

$$\text{Surface Area} = \left(\frac{m_4 - m_{3Lowest}}{m_{3Lowest} - m_1}\right) \times \frac{1}{G}, \tag{5.1}$$

where m_1 is the weight of the empty dish; m_2 is the weight of the dish plus sample; m_3 (1st) and m_3 (2nd) are air-evacuated weights; m_4 is the weight of the dish, sample and ethylene glycol; G is the weight of Ethylene glycol required to form a mono-layer over 1.0 m^2 of a solid surface = 2.8×10^{-4} gm/m^2, used as recommended by Cerato and Lutenegger (2002).

5.4 EQUILIBRIUM ADSORPTION

In order to understand more about the adsorption properties of the glass and control, a gravel standard test using methylene blue and copper solutions. (ASTM C837 – 99; 2003) was used. Copper was expected to be the most important soluble metal and methylene blue is a standard organic absorbate *(http://chemistrylaboratoryreports.blogspot.com/2010/04/adsorption-of-methylene-blue-by.html)*. Crushed glass or pea-gravel with weights between 1 gr and 5 gr were put into the conical flasks with a known concentration of either methylene blue or of copper solution. The initial concentrations of the adsorbate were measured using ICP for copper and the UV-spectrophotometer calibrated curve for methylene blue. The flasks were put in an orbital fixed-temperature shaker for measured time intervals between 10 and 120 min. After the reaction times the concentration of adsorbate was measured again.

The adsorption capacity expressed as mg/mg was then calculated from the following equation:

$$\text{Adsorption capacity} = \frac{(C_{0i} - C_i) \times V}{M}, \tag{5.2}$$

where C_{0i} is the initial concentration of adsorbate, mg/l; C_i is the concentration of adsorbate after shaking, mg/l; V is the volume of the adsorbate solution taken for the experiment, ml; M is the weight of the adsorbent, mg.

CHAPTER 6

RESULTS AND DISCUSSION

6.1 DIGESTION TECHNIQUE

It has already been shown that the variation in the dissolved fraction of the metals depends on the variability of storm events, the time of sampling (in wet or dry weather, although it is always greater in dry weather; see the data of Mosley and Peake, 2001), the type of urban area and the digestion procedure. This makes the interpretation of the analysis complex. From Table 2.2 it can also be seen that the solubility of each metal is different, which makes the interpretation of the effects of applying different digestive techniques (microwave digestion and traditional hot plate) as well as different combinations of acids more difficult.

Of specific concern in our research was the method of metal recovery applied, since microwave digestion is quicker and safer than the traditional method which uses hot plate aqua regia whereby the water samples are digested on hot plates with acidic mixtures of HCl and HNO_3 (APHA, 2005). This digestion procedure has been widely used for metal recovery from solid materials but it is a slow operation because of the need to evaporate off the acids. Moreover, open systems are used during the digestion process, which might result in atmospheric contamination and losses of volatile metal derivates during the oxidation of organic substances contained in the samples (Wong et al., 1997; Chen and Ma, 2001; Sun et al., 2001).

The microwave digestion method, which became available in 1980, is quicker, safer and more efficient and it is not susceptible to losses of volatile metals. Our results which were obtained from applying the two digestion methods to 10 samples in a dirty water matrix are shown in Table 6.1.

From Table 6.1 one can see that the hot plate aqua regia method gave recoveries in the range of 52 - 85%, which agreed well with a study by Chen and Ma (2001), where recovery of metals by aqua regia was approximately 80%. The microwave digestion method is more rigorous (since it acts at a higher temperature and uses sealed tubes) than the hot plate method, therefore it produced a better recovery of metals, apart from nickel. The amount of iron measured was also greater than the concentration found in the spiked samples (Table 6.2). This data agrees with that obtained by both Chen and Ma (2001) and Somer and Unlu (2006). Somer and Unlu (2006) suggested that for the determination of nickel, HNO_3 could not be used because of the volatility of its nitrates. Instead of HNO_3, it was suggested that $HClO_4$ and H_2SO_4 were better acids for the digestion of biological materials containing nickel. Our results are ambiguous on this point since the microwave is sealed but if volatile nitrates are generated these may be released on opening. Recovery from the microwave digestion method for Ni was worse than for the hot plate and this requires further research. Similarly, when analysing chromium, Somer and Unlu (2006) suggested that HCl was unsuitable because of the volatility of $CrCl_3$ and thus the evaporation time for Cr should be as short as possible. Tursic et al. (2008), however, also observed poor recovery of Cr (24%) when using HNO_3 and H_2O_2, but in contrast to Somer and Unlu (2006) their recovery of Cr was higher (81%) when they used HNO_3 and HCl together with HF. Sun et al. (2001) demonstrated that the use of different combinations of acid influenced the decomposition of sample matrices. Good recovery of Cr, Cu, Fe, Ni and Zn (96 –113%) was achieved using the microwave digestion method and combinations of different acids but, like Tursic et al. (2008), Sun et al. (2001) found that HF gave greater accuracy. Only small differences were found compared to open hot plate digestion (92 – 104%), where recovery was slightly

Table 6.1 Metal recovery by the two digestion methods

Pollutant	**Percentage of metal recovery from calibration standards, %**	
	Hot plate aqua regia	**Microwave aqua regia**
Fe	70 – 85	102 – 117
Cu	52 – 68	90 – 95
Zn	55 – 66	92 – 96
Pb	48 – 63	Not analysed
Cr	62 – 78	77 – 84
Ni	58 – 70	41 – 43

lower. Wong et al. (1997) reported similar findings, namely that HF improved the recovery of metals from soil, especially if the soil contained a strong silicate matrix. Thus there is a consensus in the literature which suggests that HF is an important acid which can overcome the difficulties associated with metal volatility during boiling. Unfortunately, HF is very difficult to handle and is best avoided if possible, which was why we decided not to use it.

Fig. 6.1 and Table 6.2 represent the results of the dissolved fraction for metals as well as their total concentrations obtained from the two digestion methods for the M1 and Loughborough sewage effluent (LSW). The results with basic statistics are also shown in Table 6.2.

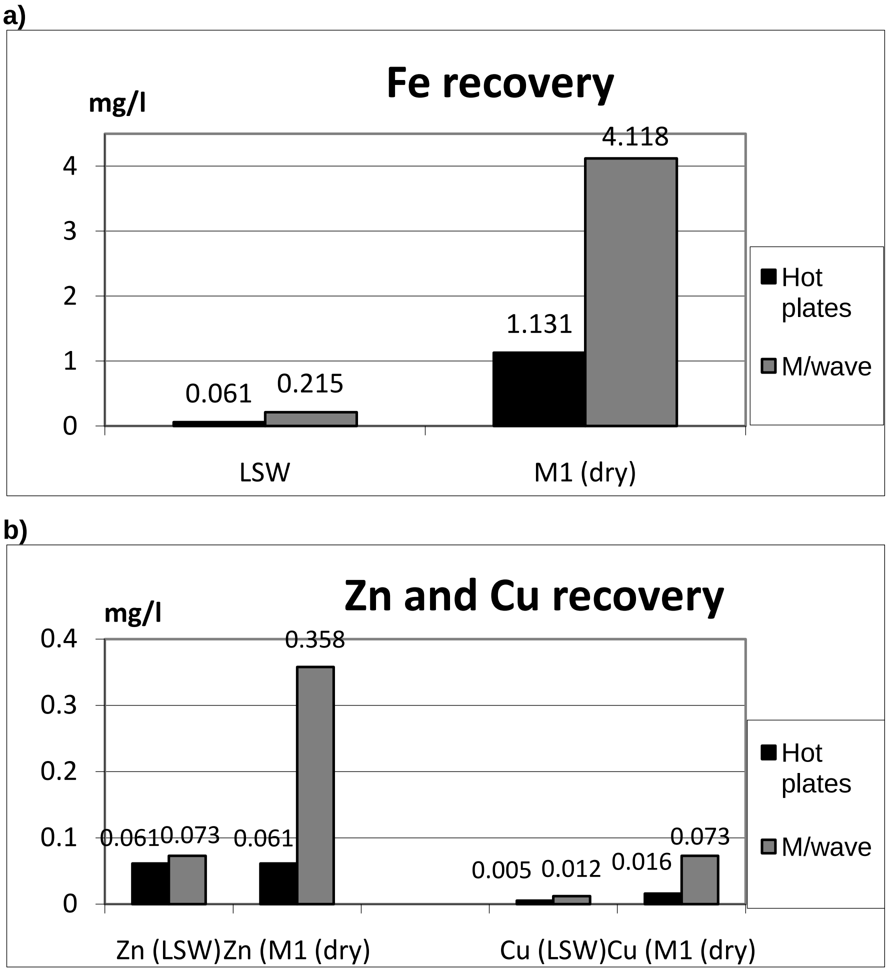


Fig. 6.1 Average values of metal recovery by the two digestion techniques

It can be seen (Table 6.2) that the f_{dis} in all cases for microwave digestion is a smaller fraction than that for the hot plate method, which supports the previous work where it was suggested that volatility losses do occur.

Table 6.2 Comparison of average dissolved metal fraction $\boldsymbol{f_{dis}}$ by the two digestion methods

Location	Fe		Cu		Zn	
	I	**II**	**I**	**II**	**I**	**II**
M1(dry)	0.17	0.11	0.56	0.26	0.49	0.34
LSW	0.5	0.18	0.8	0.4	0.83	0.6

I - hot plate; **II** - microwave digestion.
LSW (hot plates) – 8 samples (TSS 9.0 mg/l); LSW (m/wave) – 19 samples (TSS = 9.4 mg/l);
M1 (hot plates) – 32 samples (TSS = 38 mg/l); M1 (m/wave) – 40 samples (TSS = 33 mg/l)

Another feature of this data is that the metal concentrations obtained from the lagoon (M1) have a lower solubility compared to the sewage work effluent. This can be attributed to the TSS value, which was 3 times higher than that recorded in samples from the sewage works (see footnote, Table 6.2). This confirms our results, which will be described later in section 6.4 (Woodbrook), where it is shown that TSS plays an important role in metal binding. This was surprising at first since the average retention time in the lagoon is more than 20 days. It could, however, be accounted for by algal growth in the lagoon increasing the TSS, which is reported for sewage treatment (Camargo Valero and Mara, 2007).

Comparing the evidence from the two digestion methods, in application it is demonstrated that microwave digestion gives a better recovery of total metals than hot plate digestion. Microwave aqua regia digestion increased elemental recovery for iron, copper and zinc as expected, but microwave digestion recovers less chromium and nickel. This will require deeper investigation but by that particular stage in our work it had become apparent that Cr and Ni were very minor components in the runoff and their analysis was therefore suspended.

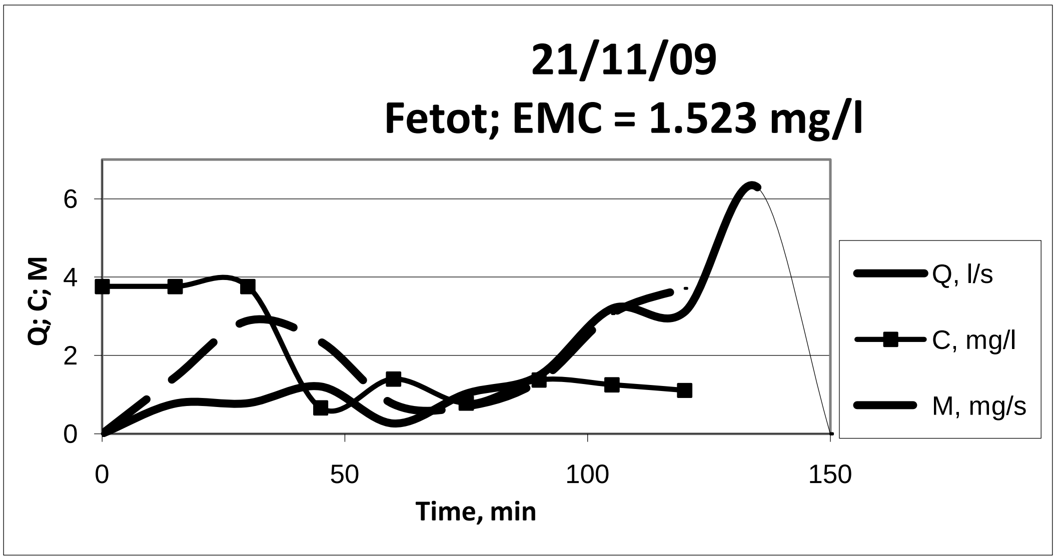
6.2 M1 (Rainfall characteristics and metals)

6.2.1 First Flush Behaviour

Figure 6.2 shows a hydrograph and a pollutograph of Fe_{tot} for two complete rainfall events at the M1 for sampling point 1 (see Fig. 4.2 b). The period which was sampled for the hydrographs is shown in bold, whereas the unsampled tail of the storms is shown in the thin line, which represents flow only.

The Fe_{tot} concentration for storm 1 (Figure 6.2 a) was 3.76 mg/l at the beginning of the rainfall event but it decreased as a result of dilution as the flow rate rose during the storm, reaching 1.2 mg/l after 120 min. In the second event (Fig. 6.2 b) the concentration was lower at the start of the rainfall event (0.6 mg/l) and it was unaffected by the increase in flow rate.

a)



b)

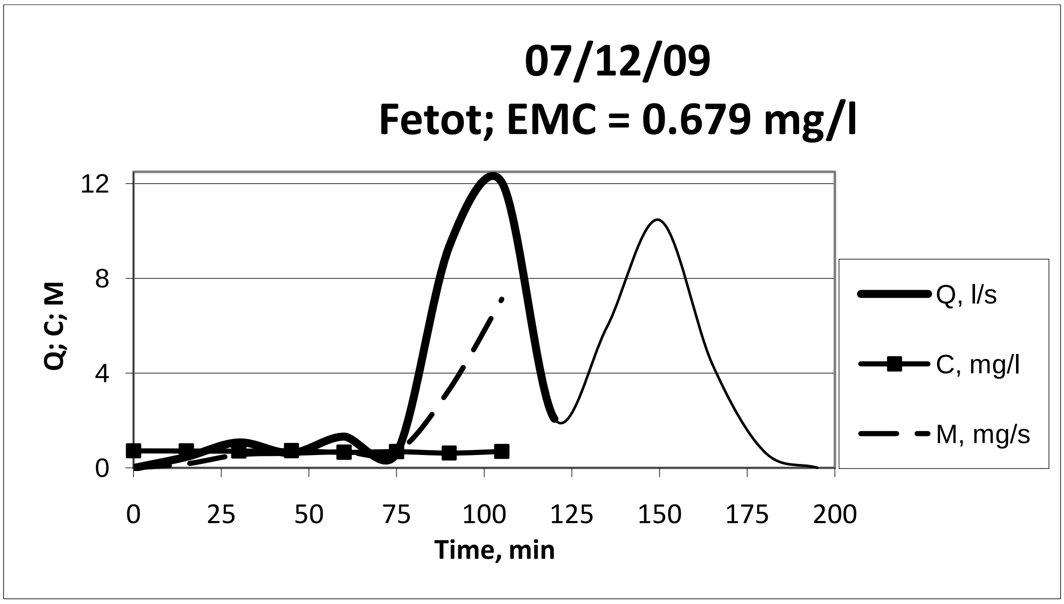


Fig.6.2 Hydrograph, pollutograph and mass-pollutant graph for two rainfall events obtained for Fe_{tot}

A mass balance of the pollutants in the first 30% of the runoff volume is summarised in Table 6.3.

Table 6.3 Pollutant mass in the first 30% of the runoff volume

Pollutants	Pollutant mass, %	
	21/11/2009 (peak flow 3.2 l/s)	07/12/2009 (peak flow 12.1 l/s)
TSS	39.7	19
TOC	29.5	17.4
Fe_{tot}	45.3	17.3
Fe_{dis}	73.6	19.5
Zn_{tot}	43.3	14.8
Zn_{dis}	28.8	14.1
Na	29.5	15.4

In the case of the first storm (Fig. 6.2 a) the rainfall was 2 mm and followed a 2-day dry period. The second storm (Fig. 6.2 b) was 2 mm and occurred in a period of continuous rainfall. The peak flow for storm 1 (Fig. 6.2 a) was a quarter of that for storm 2 (Fig. 6.2 b). The time of entry for both storms was about 75 minutes but with different peak times (Fig. 6.2), suggesting the importance of rainfall intensity.
When integrating the mass of iron discharged, an example indicated 16.2 grams for storm 1 (Fig. 6.2 a) and 15.6 grams for storm 2 (Fig. 6.2 b).

On the basis of their data, Wanielista and Yousef (1993) (cited in Davis and McCuen, 2005) suggest a definition of 'first flush' as occurring when 50% of the mass is present in the first 25% of volume. Bertrand-Krajevski et al. (1998), on the other hand, propose a definition of 'first flush' as occurring when 80% of the mass pollutants are present in the first 30% of runoff volume.

Figure 6.3 shows the same data as a cumulative mass fraction for both events.
The first flush effect was pronounced in the 21/11/09 event. The pollutants which displayed these characteristics most strongly were TSS, Fe_{tot}, Fe_{dis} and Zn_{tot} which is represented by the non-linear graph as shown in Figure 6.3 b, c, d and e.

The 21/11/2009 rainfall event showed more than 40% of Fe_{tot}, Zn_{tot} and TSS discharging within the first 30% of the runoff volume (see Table 6.3). The Fe_{dis} showed its highest level of mass, 73.6%, in the first 30% of the runoff volume. This

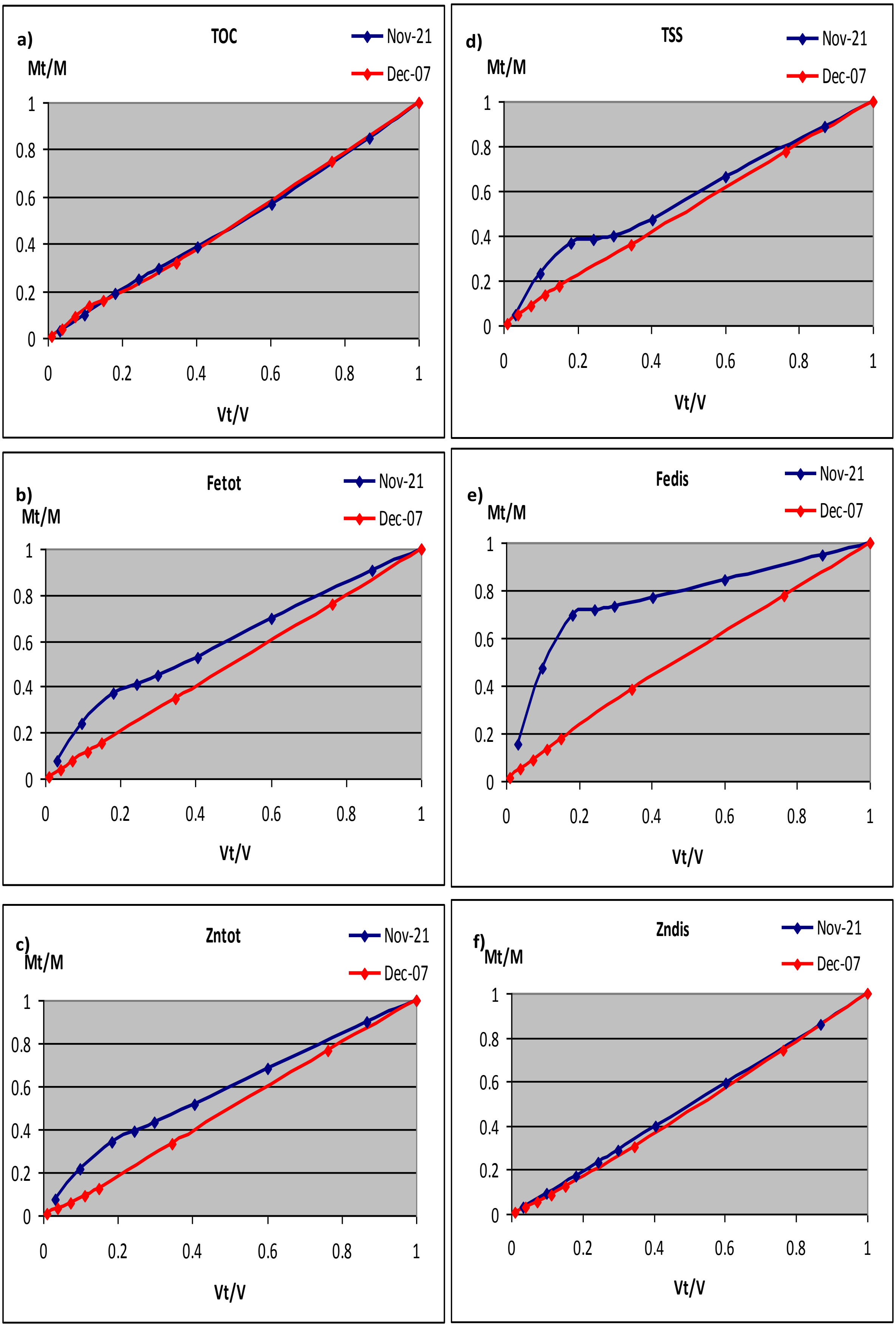


Fig. 6.3 First flush characteristics of selected parameters

was the only pollutant which met the criteria for a first flush that were suggested by Wanielista and Yousef (1993) or Bertrand-Krajevski et al. (1998). Other dissolved components (Na, TOC and Zn_{dis}) did not demonstrate these first flush characteristics.

These data (Fig. 6.3) confirm that TSS and associated metals behave differently compared to dissolved pollutants, as might be anticipated from basic transport theory. Prestes et al. (2006) also reported on the effects of storm duration on levels of TSS, which diminished as the event progressed. They deduced from their analysis that a 10-day ADWP yielded a more than 30-fold increase in TSS levels in urban runoff.

The second event observed on 07/12/09 showed linear characteristics, the concentration of the pollutant having been directly proportional to the volume, and there was no indication of first flush. The only parameter which appears to be non-linear from this event is TOC, as shown in Fig. 6.3 a and Appendix 4.

Berretta et al. (2008) found some signs of first flush behaviour when measuring TOC (mainly soluble), but this was not linear. In a similar way to our study, TSS also exhibited first flush characteristics but Zn_{dis} did not. Giulianelli (1988) suggested that first flush levels for TSS were more pronounced in urban areas due to the runoff's washing roof tops and the greater road area. The other components, TOC and Zn_{dis} did not display these characteristics.

Thus, it can be concluded that ADWP, rainfall intensity and the phase of the pollutants all influence the outcome as to whether a first flush of contaminant is observed.

As noted, an accumulation of sediments was observed in the inlet and drains at the sampling site. During dry weather, because of evaporation, TSS concentration increases as well as total metals. More complicated equilibria and re-solubilisation may take place and are suggested for iron in particular, which is more soluble anaerobically. This may enhance the ‘first flush’ effect for Fe_{dis} following ADWP, as seen in Fig. 6.3.

6.2.2 Metals

Table 6.4 is a summary of the data obtained from the lagoon during dry weather (April 2008 – December 2009) and Table 6.5 summarises the corresponding data during wet weather (7 events), limited by or defined as when there was sufficient rainfall to cause actual discharge from the separator into the lagoon itself. Raw data of metal concentrations and other water quality parameters are presented in Appendices 5 and 6.

Dry weather samples were taken from the lagoon itself as close to the inlet as possible and wet samples were taken from the inlet as it flowed into the lagoon [as noted in the Methodology section (4.1.1)]. Comparing these tables it can be seen that the concentrations of TSS and Fe_{tot}, in some cases, were higher during dry weather than those obtained during rainfall events. This can be explained by evaporation: for example, in May 2008 samples were taken during an extended dry-weather period (ADWP 16 days). September 2008 was also an unusually dry month (22.4 mm) and samples were taken within the dry period. The most striking results were those obtained in September 2009 when the water levels in the SuDS lagoon were the lowest observed because of evaporation. Table 6.6 shows a selection of the dry weather parameters from which the extreme (unusual) data has been excluded. The mean values of Fe_{tot}, TSS, Turbidity, PO_4^{3-} and NO_3^- then decrease by more than half. This improves both the SD and coefficient of variation, but SD is still greater than the mean values. Thus, with this long dry weather data removed, the common pollutants are approximately 3 times greater in wet weather, which is similar to the level suggested from the literature and predictive models.

During November and December 2009 there was very wet weather with continuous rain (which coincided with widespread flooding in the North West). On the 20/11/2009 the amount of rainfall that fell in Cockermouth, Cumbria was 316.4 mm over 24 hours with a total rainfall for November of 1024 mm

Table 6.4 Data from the lagoon during dry weather conditions

Contaminant, mg/L except pH, turbidity and EC	Range	$\overline{X}$	S	C_v
Iron (total) **(59 samples)**	0.112 – 7.386	1.119	1.577	1.41
Iron (dissolved) **(59 samples)**	0.004 – 0.321	0.103	0.071	0.689
Copper (total) **(59 samples)**	Traces – 0.041	0.005	0.009	1.8
Copper (dissolved) **(59 samples)**	Traces – 0.016	0.002	0.003	1.5
Zinc (total) **(59 samples)**	Traces – 0.215	0.057	0.045	0.789
Zinc (dissolved) **(59 samples)**	Traces – 0.098	0.012	0.019	1.583
Na(59 samples)	26 – 936.2	139.28	171.74	1.23
pH(59 samples)	6.7 – 8.42	7.27	0.38	0.053
TSS(59 samples)	3 – 341	32.19	55.21	1.715
Turbidity, NTU **(59 samples)**	0.188 – 146	18.41	26.43	1.436
TDS **(59 samples)**	80 – 3480	492.9	631.8	1.282
EC, µS/cm **(59 samples)**	150 – 8500	942.5	1330.7	1.412
TOC **(59 samples)**	2.51 – 62.98	10.76	8.19	0.761
Hardness **(56 samples)**	70 – 500	138.7	84.7	0.611
PO_4^{3-} **, as** P **(45 samples)**	Traces – 7.831	0.88	2.01	2.284
NO_3^- **(45 samples)**	Traces – 23.8	2.87	4.24	1.477

Table 6.5 Stormwater data from the M1 during storm flow (rainfall events) conditions

Contaminant, mg/L except pH, turbidity and EC	Range	$\overline{X}$	S	C_v
Iron (total) **(36 samples)**	0.498 – 6.162	2.104	1.726	0.82
Iron (dissolved) **(36 samples)**	0.04 – 0.397	0.124	0.155	1.25
Copper (total) **(36 samples)**	Traces – 0.253	0.045	0.058	1.29
Copper (dissolved) **(36 samples)**	Traces – 0.042	0.008	0.010	1.25
Zinc (total) **(36 samples)**	0.068 – 0.312	0.141	0.065	0.461
Zinc (dissolved) **(36 samples)**	0.018 – 0.074	0.037	0.012	0.324
Na **(34 samples)**	26 - 655	86.17	117.2	1.36
pH **(34 samples)**	6.9 – 7.63	7.17	0.21	0.029
TSS **(34 samples)**	6 – 179	54	50.33	0.93
Turbidity, NTU **(34 samples)**	10.1 – 221	60	50.64	0.844
TDS **(34 samples)**	110 – 1980	340	354.9	1.044
EC, µS/cm **(34 samples)**	230 – 3760	675	707.2	1.047
TOC **(31 samples)**	2.79 – 82.86	17.19	19.615	1.141
Hardness **(26 samples)**	85 – 355	175	60.3	0.345
PO_4^{3-} **, as** P **(25 samples)**	Traces – 7.79	1.33	2.79	2.09
NO_3^- **(25 samples)**	Traces – 16.205	3.74	4.68	1.25

(*www.environment-agency.gov.uk/*). In our case, because of the prolonged wet weather, some unusual data were obtained.

The pollutants measured in those samples were very low, since November and December 2009 were exceptionally wet. Rainfall at the M1 site for the equivalent November period was 70.4 mm (see Appendix 1 for details). These conditions kept the M1 flushed of pollutants and dilution within the lagoon. Thus, the rainfall event observed on December 7th (8 samples) had very low TSS and metal concentration, which affected the whole set of wet weather results. Table 6.7 represents the data without this event. Thus, analysing the differences between Tables 6.4 and 6.6 and Tables 6.5 and 6.7 one can see that extreme weather conditions affect statistical means and the reliability of the interpretation of the results.

Table 6.6 Data from the lagoon during dry weather conditions (excluding the continuously dry days during September 2009)

Contaminant, mg/L except pH, turbidity and EC	Range	$\overline{X}$	S	C_v
Iron (total) (52 samples)	0.112 – 4.87	0.77	0.852	1.106
Zinc (total) (58 samples)	Traces – 0.188	0.054	0.013	0.241
TSS (52 samples)	3 – 82	16.097	13.9	0.863
Turbidity, NTU (52 samples)	0.188 – 98.8	14.26	18.69	1.311
TOC (58 samples)	2.51 – 20.569	9.86	4.52	0.458
PO_4^{3-} **, as** P **(41 samples)**	Traces – 1.567	0.3	0.672	2.24
NO_3^- **(42 samples)**	Traces – 5.67	1.89	1.54	0.815

Table 6.7 Data from the M1 during wet weather conditions (excluding the rainfall event on December 7th 2009)

Contaminant, mg/L except pH, turbidity and EC	Range	$\overline{X}$	S	C_v
Iron (total) (28 samples)	0.498 – 6.162	2.505	1.763	0.704
Zinc (total) (28 samples)	0.079 – 0.312	0.157	0.067	0.427
Cu (total) (28 samples)	Traces – 0.253	0.058	0.06	1.034
Cu (dissolved) (28 samples)	Traces – 0.042	0.011	0.011	1.0
TSS (26 samples)	6 – 179	67.305	50.599	0.752
Turbidity, NTU (26 samples)	10.1 – 221	71.67	52.707	0.735
TOC (23 samples)	5.85 – 82.86	21.135	21.252	1.01

Tables 6.4 and 6.5 show that the coefficient of variation C_v of measured water quality data has a much wider value than in Tables 6.6 and 6.7, from which the extreme events have been excluded.

Wu et al. (1998) presented results of variance in samples of pollutant loading for runoff from three highways in the City of Charlotte (North Carolina). Table 6.8 summarises the information about site characteristics as well as the coefficients of variation of some pollutants. In this study traffic flow values are less than 2% of those on the M1 but the C_v values are similar.

Table 6.8 Characteristics of highway runoff testing sites and coefficient of variation C_v with mean values $\overline{X}$ *

Site	Type	ADT	Road surface	Coefficient of variation C_v Mean $\overline{X}$					
				TSS	TDS	NO_{3+2}-N	NH_3-N	TP	Cu
I	urban	25,000	concrete/ asphalt	0.76	0.93	1.84	0.45	1.04	0.7
				283	157	2.25	0.83	0.43	0.024
II	urban	21,500	asphalt	0.69	0.54	0.62	0.28	0.82	0.5
				93	88	0.22	0.76	0.52	0.012
III	urban	5,500	asphalt	1.07	1.26	1.15	0.63	0.86	0.6
				30	216	0.14	0.52	0.47	0.005

* modified from Wu et al. (1998)

From this table one can see that the coefficients of variation were in the range from 0.28 to 1.84. Such wide fluctuations of C_v can be explained by the fact that samples during wet weather were collected at different times during the rainfall events and the latter had different characteristics (ADWP; rainfall intensity and duration). Our data for C_v for Cu_{tot}, for example, was two times higher ($C_v = 1.29$; Table 6.5) compared to Wu et al. (1998) (site I). One possible explanation is the number of observed events: 10 events in their case and 5 in our case, which means that the C_v would be biased by unusual storm events. The concentration values in their case were half those found in our data (Cu_{tot} = 0.45 mg/l; Table 6.5), which can be explained by either the lower traffic flow, even at site I, or our use of microwave digestion. Comparing the C_v for TSS one can see that Wu's data corroborate those found from the M1, although the concentration values were much higher, implying that the sampling location as well as the local catchment conditions are important when interpreting the results.

Gunderson et al. (2001) have also noted that the time of sampling within the storm event was crucial to the result because of both the first flush effects and the reverse, where samples taken after long steady rain diluted the concentration. Therefore the time of sampling and method of sampling is an important influence on the result. If climate change gives rise to more extreme weather then the EQS may need to take into account the effect of, for example, a prolonged dry period.

Taking the mean values (Tables 6.4 – 6.7), for all conditions and species, then Fe was always found to be present at the highest concentrations, as the most ubiquitous element in both soil and the urban environment. The Fe solubility was the lowest among the metals during both dry and wet weather, i.e. 9.2% and 5.89 % respectively (Fig. 6.4).

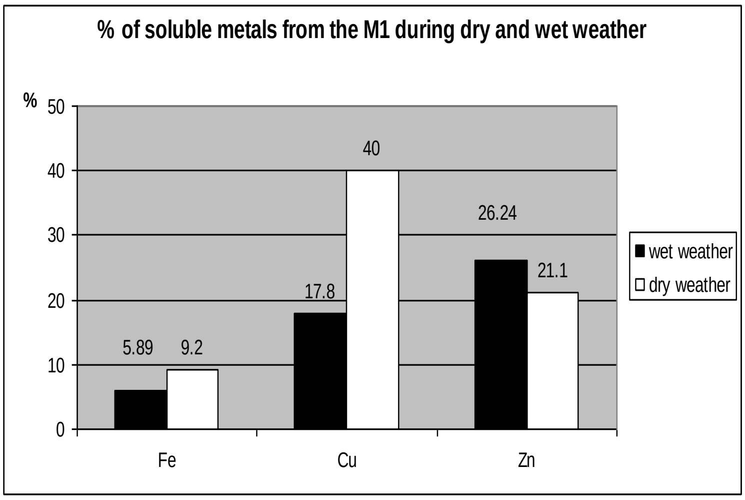


Fig. 6.4 The solubility of the indication metals

There is little information to compare with the literature (see section 2.4) because the toxicity of Fe is low and it occurs in amounts which are still small compared to the background and EQS (Fe_{dis} = 1 mg/l). For example, Mosley and Peake (2001) reported that the concentration of Fe_{dis} during wet weather was 0.211 mg/l and during dry weather (background concentrations) 0.243 mg/l. The average concentration from the M1 during wet weather was 0.124 mg/l (Table 6.5) and 0.103 mg/l during dry weather (Table 6.4).

Hallberg et al. (2007) found the same order in metal concentrations (as shown in Tables 6.4 and 6.5), that is Fe>Zn>Cu, from their study of the seasonal variations of metals in highway runoff from a trunk road in Stockholm. Their values are much higher than ours because of the different drainage systems and the more extreme cold weather. For example, in winter the TSS concentration in runoff in Stockholm reached 1500 mg/l, with a maximum value of around 5000 mg/l and Fe_{tot} of 226 mg/l, as a result of applications of de-icer. The average for Fe_{tot} in our results during wet weather was 2.104 mg/l (Table 6.5). Despite these large values of Fe_{tot}, and in common with our results, the Fe_{dis} in their study did not exceed 1 mg/l (with a maximum value 0.57 mg/l), confirming its very low solubility and therefore low toxicity.

Potential chemical mechanism to explain the reduction in hardness

Throughout the period of study it was observed that the release of Fe_{dis} in the lagoon was coupled with a decrease in the level of hardness and TDS, compared to the inlet (see Fig 6.5).

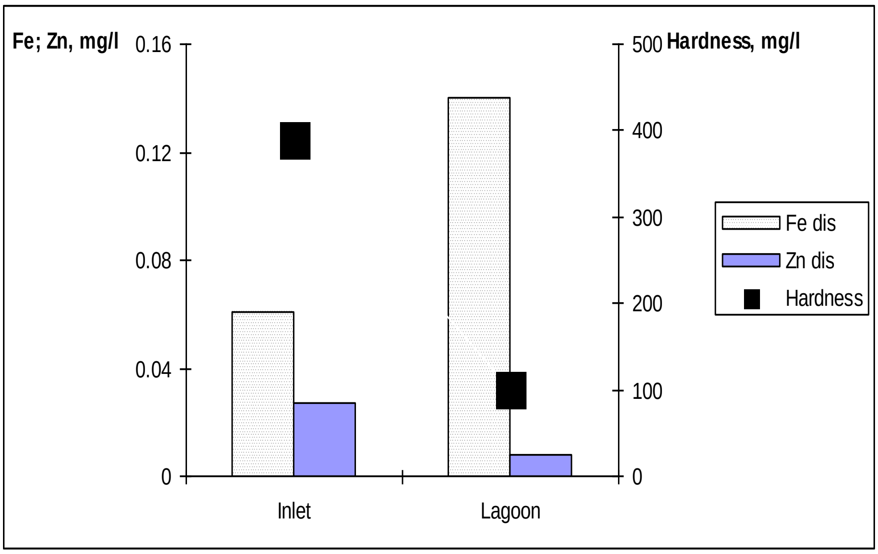


Fig. 6.5 Metals and hardness profile (average results from the period of October-December 2009)

Another observation made on site during the sampling was the fluctuation of water levels in the treatment system because of the dry and wet weather periods. It is suggested that this could result in alternating aerobic and anaerobic conditions and therefore iron reduction and oxidation (ferrolysis) in particular, which was reflected in the measured hardness.

During wet periods, Fe $(OH)_3$ undergoes reduction, with organic matter supplying the electrons:

$$Fe(OH)_3 \xrightarrow{e^-} Fe(HCO_3)_2 \tag{6.1}$$

The above-written reaction takes place both in the inlet and in the lagoon, thereby reducing the hardness.
Once the surface drains, aerobic conditions prevail again, oxygen is in excess, and Fe^{2+} re-oxidises and generates acidity:

$$Fe^{2+} \xrightarrow[O_2]{} Fe(OH)_3 + 2H^+ \tag{6.2}$$

When the $Fe(HCO_3)_2$ has been formed, the spatial separation of Fe^{2+} might be more soluble, as can be seen from Fig. 6.5 which links the release of the Fe_{dis} with the decrease in the hardness. This process will probably take place only if the conditions permit the HCO_3 formed from atmospheric CO_2 to filtrate through the sediment profile, which was not possible in the inlet because of the concrete site. Schematically the process of iron release is diagrammed in Table 6.9.

However, this needs more study, specifically by means of a well-controlled laboratory experiment to monitor HCO_3 and redox potential.

Table 6.9 Iron release process

Inlet	**Lagoon**
$Fe^{2+} \xrightarrow[O_2]{} Fe(OH)_3 + 2H^+$ $Fe(OH)_3 \xrightarrow{e^-} Fe(HCO_3)_2$	$Fe^{2+} \xrightarrow[O_2]{} Fe(OH)_3 + 2H^+$ $Fe(OH)_3 \xrightarrow{e^-} Fe^{2+} + HCO_3^- \downarrow leaching$

The next commonest metal was Zn and its solubility during wet weather was slightly higher than during dry weather (26.24% and 21.1%, respectively). It is suggested that the solubility of Zn depends on the presence of salts, which releases it from the sediment particles (sludge, silt) by an ion exchange mechanism. A similar principle is used in the sequential speciation analysis for the analysis of metals from soils (Stover et al., 1976). Figure 6.6, as an example, shows the percentage of dissolved Zn and Fe with Na concentration in samples taken during dry weather, from the three separate chambers of the interceptor.

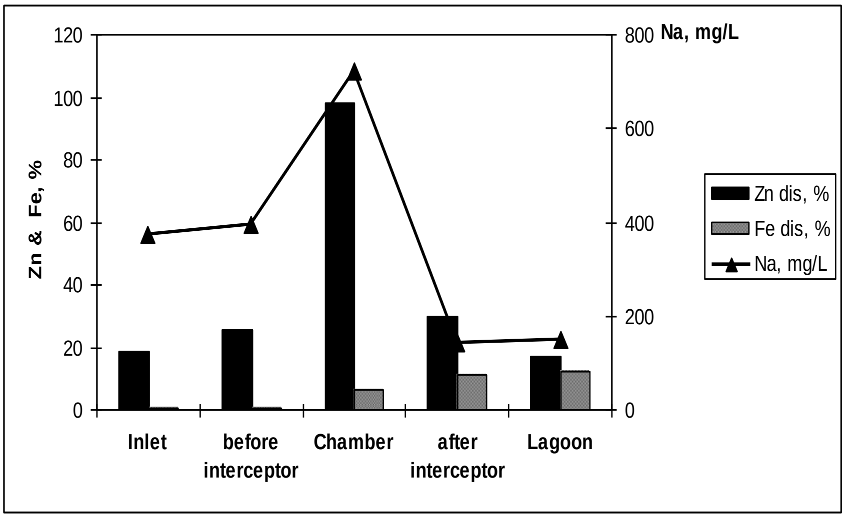


Fig. 6.6 Metal profile through the SUDS system during a cold winter storm, 13/01/2009 (single samples Zn_{tot} is 0.155 mg/l in the holding chamber with 9.0 mg/l TSS)

There is a distinctive peak of Zn and Na in the holding chamber of the separator. The peak in salt was likely to be as a result of de-icer applications. The dissolved Fe does not follow the Na pattern and it is suggested that this is because of iron's lower solubility.

This behaviour was taken as further evidence that a disturbance to the equilibrium between soluble and precipitated metals could occur and could lead to the re-solubilisation of some metals. In this case the disturbance was by high concentrations of dissolved salts (sodium), indicating an ion release mechanism rather than redox as suggested with iron. The Zn_{dis} concentration was 98% of the total (Zn_{tot} 0.155 mg/l in the chamber [Figure 6.6] with 9.0 mg/l TSS). For a comparison, "after the chamber of the interceptor" without flow the dissolved zinc concentration was 30% of the total with 7.0 mg/l TSS.

Another example event (Fig. 6.7) shows that the increase in Zn solubility from 50 to 80% was linked to the Na concentration during a storm rather than snap grab, illustrating a long-term pollutant input. Nelson et al. (2009) also reported that the presence of NaCl resulted in a large release from copper, but in our study there was no effect on the Cu, probably because Cu concentrations were too low. Nelson et al. (2009) suggested a number of mechanisms for mobilisation, such as cation exchange, chloride complex formation and colloid breakdown or dispersion, with released organic matter and/or clay complexes.

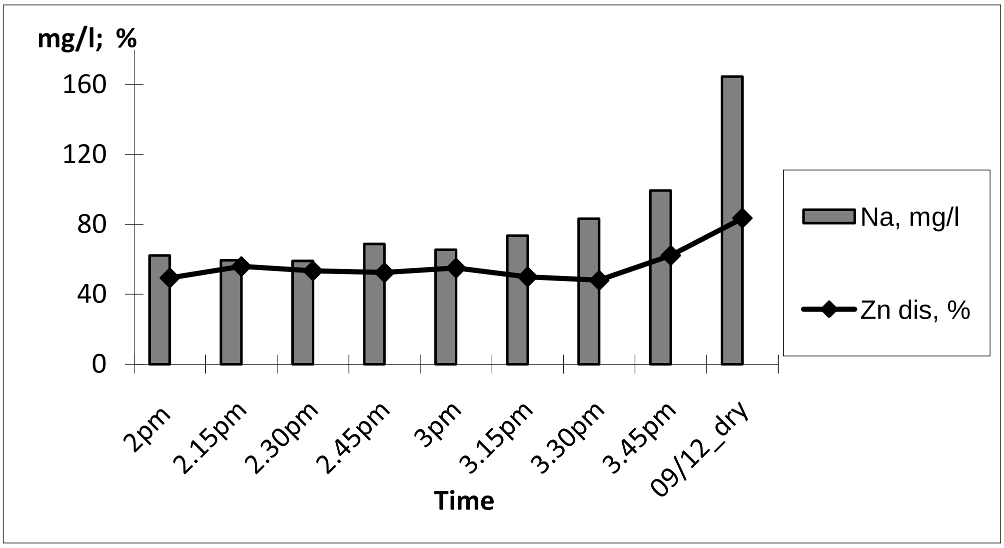


Fig. 6.7 Dissolved Zn profile during the rainfall event on the 07/12/09 and during dry weather on the 09/12/09 (1st sampling point [see section 4.1.1]).

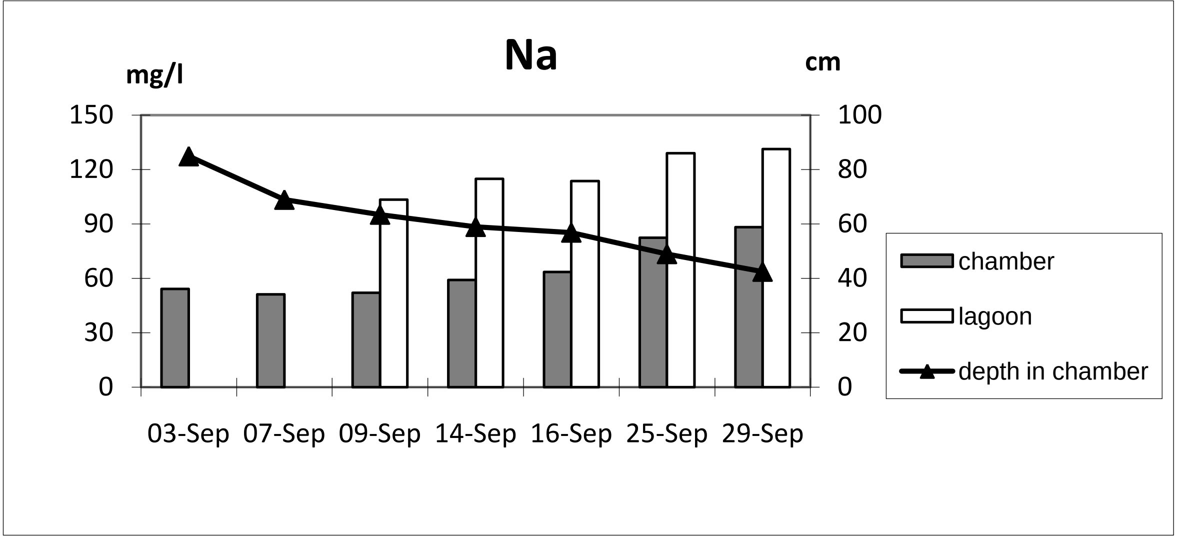
In our study Zn was the only metal released by Na. This can be explained by the fact that the Fe is bound to soil organic matter more strongly than Zn (McBride 1994). This has also been noted in work on the sequential extraction of metals from soils (Stover et al., 1976).

Copper concentrations were lower than those of the other metals. Cu concentration varied widely, from negligible to values which exceeded the EQS (0.01 mg/l for hardness 150 – 200 mg/l). The maximum value of the Cu_{dis} in the lagoon (in dry weather) was 0.016 mg/l and 0.042 in the inlet (during wet weather), and the average hardness was 138.7 and 175 mg/l, respectively (Tables 6.4 and 6.5). The behaviour of Cu was unpredictable: its solubility ranged from 18% during wet weather to 40% during dry weather. Copper is generated during braking and greater values were reported by Hulscotte et al. (2007) from an urban environment. There are other reasons for the instability of Cu: its mid-position in the transition table enables it to form more complexes. It has been reported, for example, that copper changes during storage probably by adsorption and this is explored further in the adsorption section (see section 6.6). Special sample preservation for copper, therefore, is needed (APHA, 2005). Samples were not filtered and acidified immediately (at the field sample points). This was excluded because of safety considerations, lack of power and also to avoid sample contamination during field-filtration. It is now recommended that this decision be reviewed.

Fig. 6.8 shows the water quality parameters together with the water level in the separator chamber for samples taken during September 2009 (which was exceptionally dry) from the chamber and the lagoon. As the depth decreased, so the Na increased (Fig. 6.8 a) due to evaporation from the large surface area (2000 m^2).The water level in the separator also decreased by evaporation. This was calibrated in the separator since the volume was known accurately. So, if the water level dropped from 85 cm to 40 cm, for example, the expected increase in Na concentration would be from 58 mg/l to around 120 mg/l, rather than the measured 85 mg/l, but this simply suggests that the model is more complex and should take account not only of evaporation but also adsorption and complexation. A similar increase in TSS and total metal concentrations (Fig. 6.8 b and c) can be seen in the data but in this case the TSS increase as a consequence of algal growth. The dissolved metals also increase as a result of evaporation (Fig. 6.8 d and e). However, this can be explained by the observed algal growth. The prolonged dry and sunny weather and evaporation also resulted in an accumulation of nutrients (NO_3^- and P , at 16.2 mg/l and 7.8 mg/l respectively occurred in their maximum observed concentrations).

This caused eutrophication when the water became turbid because of the algae, giving a green and brown colour to the water. So, at that time towards the end of

a)



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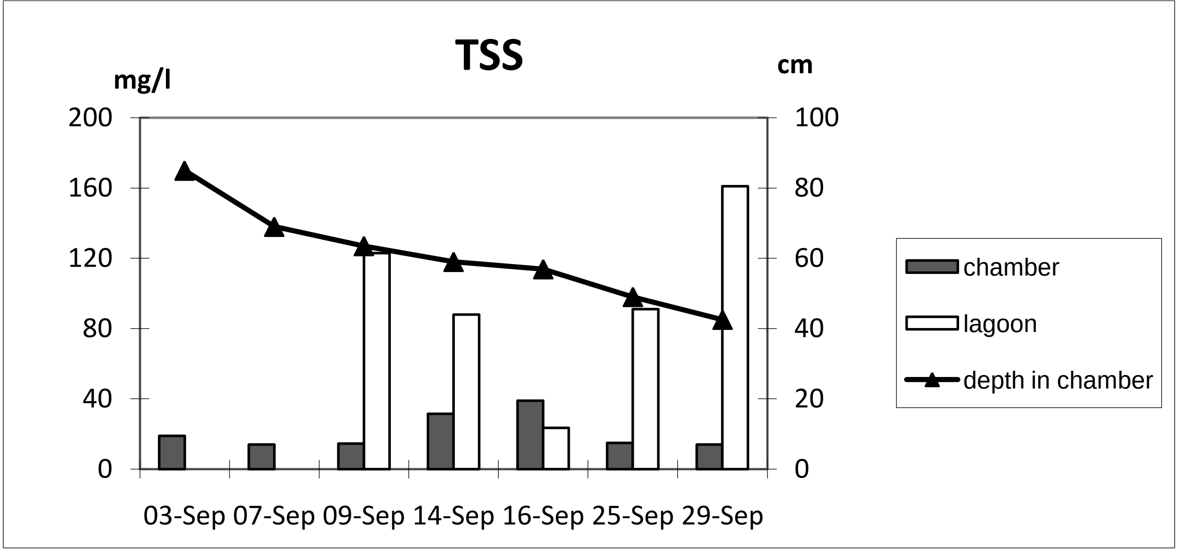

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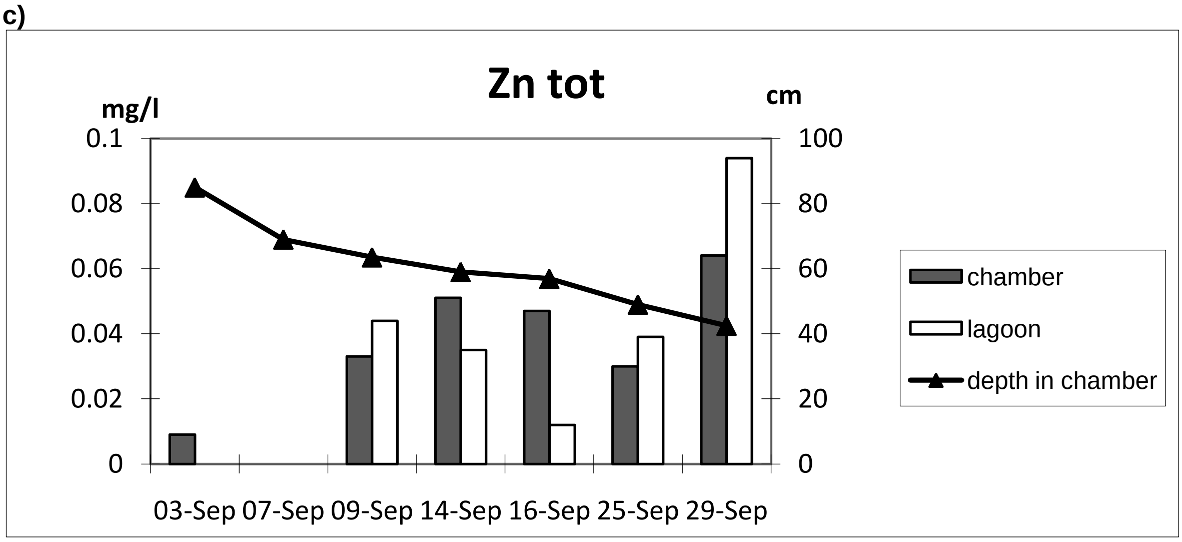


Fig. 6.8 (a; b; c) Water quality parameter changes with water level decrease

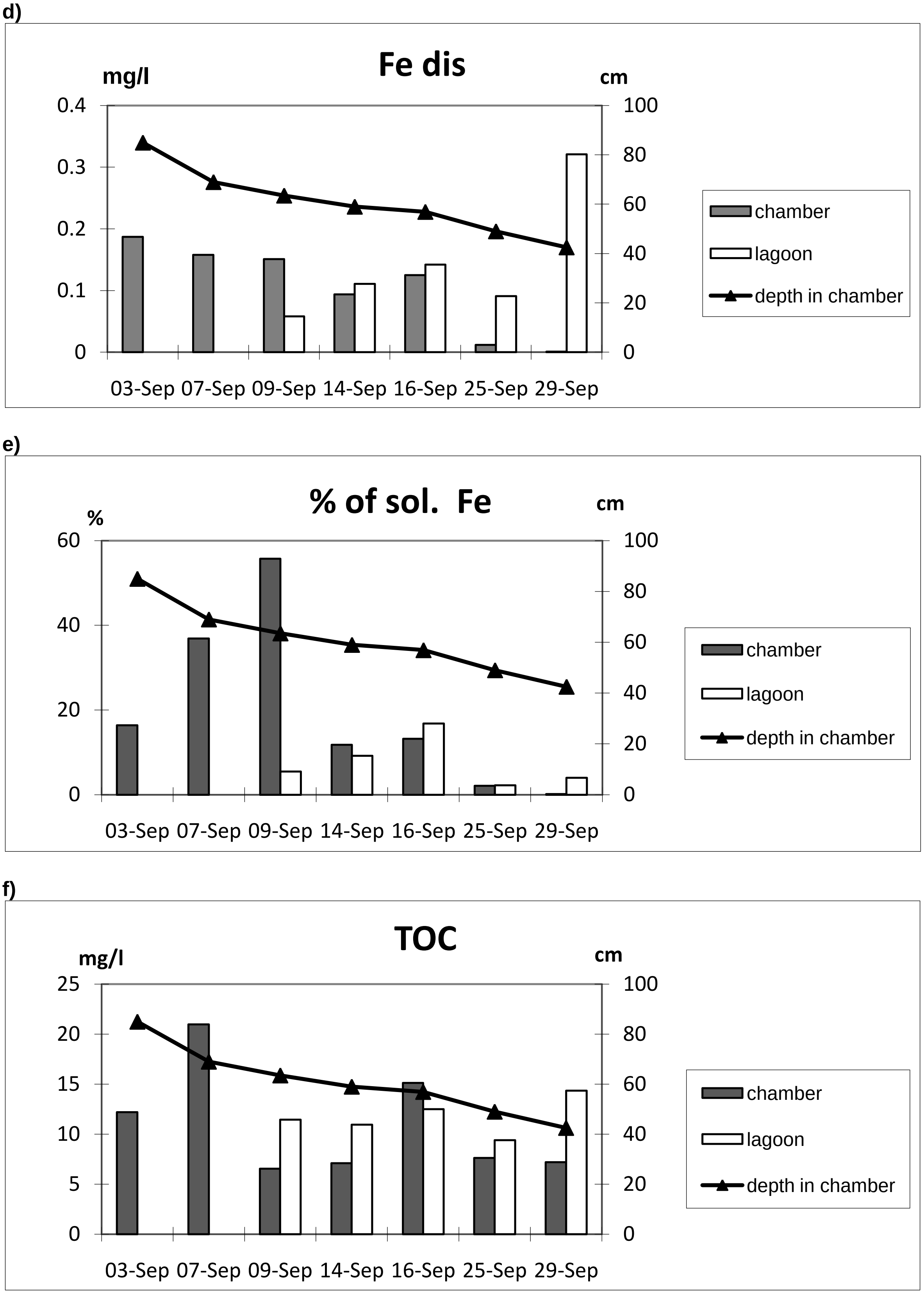


Fig. 6.8 (d; e; f) Water quality parameter changes with water level decrease

September a significant proportion of TSS in the lagoon and separator was due to algal biomass which must therefore show different adsorption behaviour compared to the TSS from dust, silt and soil particles from the highways. It was observed that biomass did not settle as dust particles did. Algae are buoyant because of their active gas production. The concentration of the algal cells increased with temperature and sunlight but then decreased at the end of the month, probably because of grazing activity and the onset of autumn rains.

Fig. 6.9 investigates possible correlations between TSS and total metals (Fe, Zn and Cu). Figs. 6.9 a, c, e show the wet weather samples taken from the M1, whereas Figs. 6.9 b, d, f show both the M1 and the Woodbrook wet weather samples added together.

Comparing the two sets of data, it can be seen that a better correlation was obtained from the same site, rather than mixing together data from two sites. This provides a potential explanation for the results reported by Crabtree et al. (2008) (see also section 2.4), who were mainly interested in copper and reported the only link between Cu_{tot} and TSS. Crabtree et al. (2008) put together 30 different sites around the UK with different characteristics. Their reported R^2 value was 0.2828 between TSS and Cu_{tot}, for example. Our equivalent data show that Cu_{tot} has the poorest correlation with TSS among other metals, from the M1 (R^2 = 0.54), but the correlation became even worse when the M1 and the Woodbrook data were put together (R^2 = 0.095). Copper was the worst link and iron the strongest and, as already noted, this reflects the reactivity and low concentrations of copper. In contrast, Desta et al. (2007) sampled only 3 sites from the Dublin ring road and analysed 42 rainfall events. They found good correlations between TSS and Cu and Zn (R^2 = 0.92 and 0.94 respectively). It is suggested that a good correlation was achieved due to the fact that the mean values for Cu and Zn from one of the sampling sites were 0.12 and 0.66 mg/l, respectively, which was much higher than our data (0.045 and 0.141 mg/l, respectively). These were caused by the urban characteristics of the Dublin ring road, particularly its stop/start junctions. Our results for the TSS and total metal correlation, when supported by Desta et al.

(2007), demonstrate the importance of achieving solid separation in stormwater management.

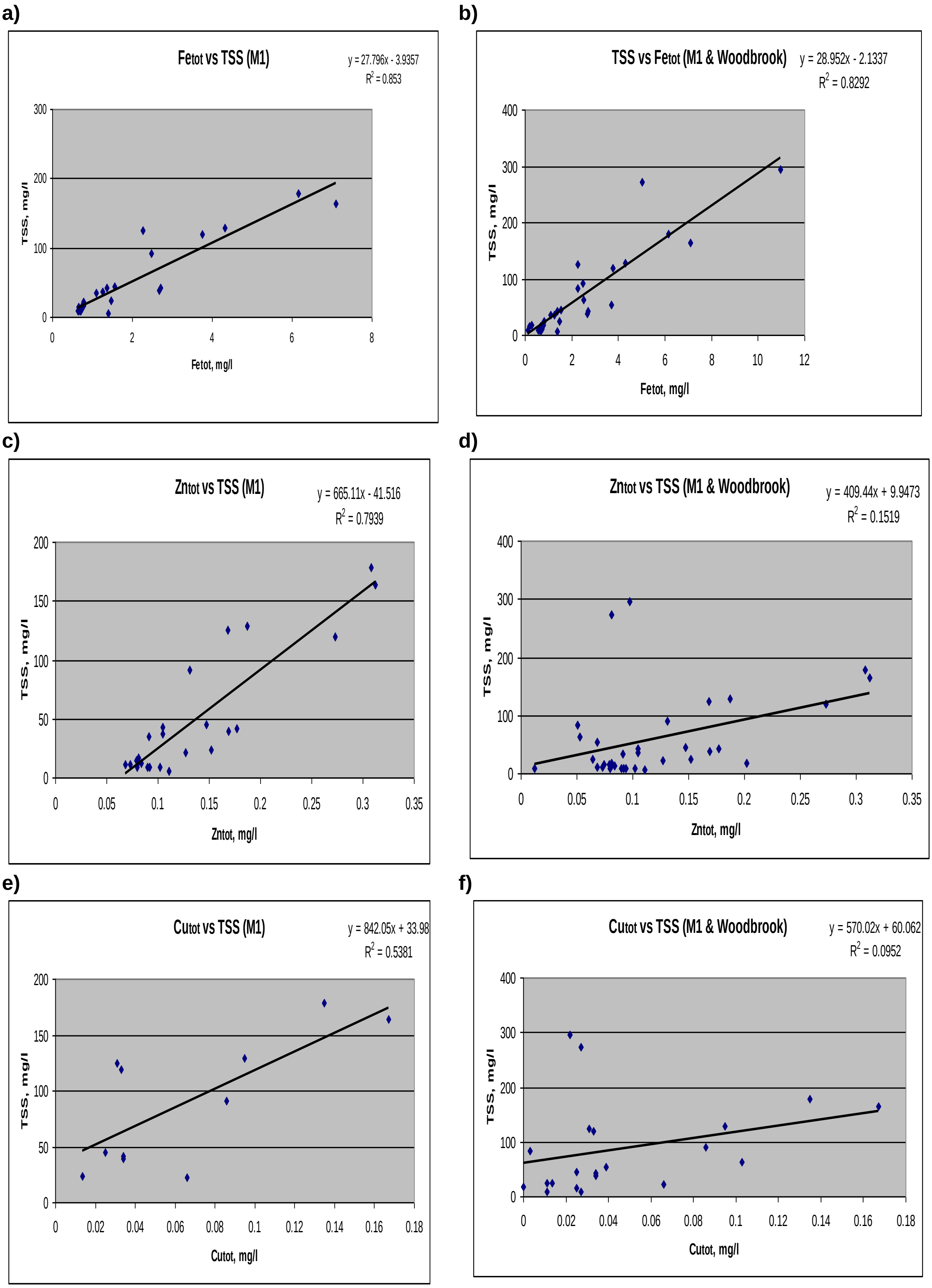


Fig. 6.9 Correlation between TSS and metals

In order to investigate further the influence of solids on metal load, two additional experiments were conducted. One experiment was designed to monitor the links between solids and metals during a storm and the second experiment was aimed at monitoring the performance of the interceptor.

Links between solids and total and dissolved metals

These data are shown in Fig. 6.10 and they not only support the existence of the trend between total metals and TSS but also show the changes in metals and TSS entering the M1 lagoon after the interceptor during the 09/09/08 storm event. The rainfall characteristics of that event are shown in Table 6.10.

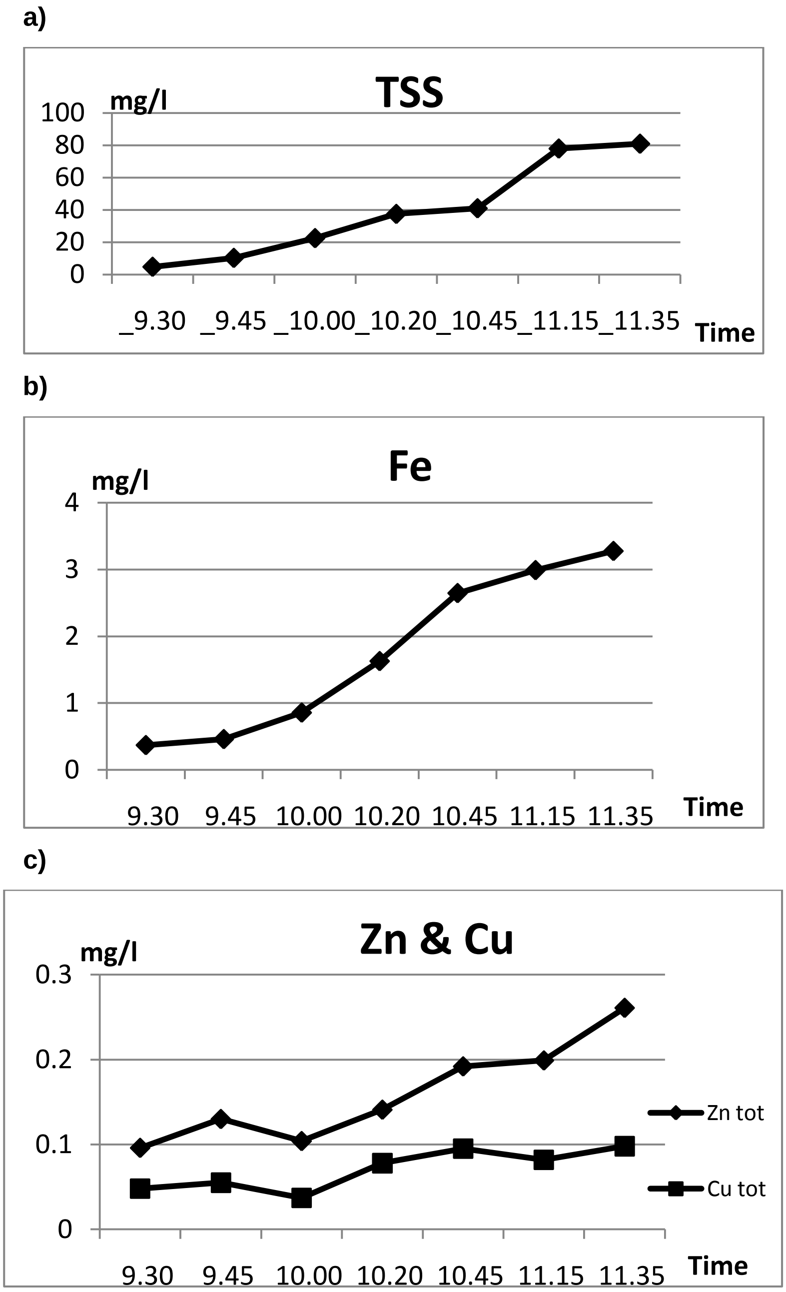
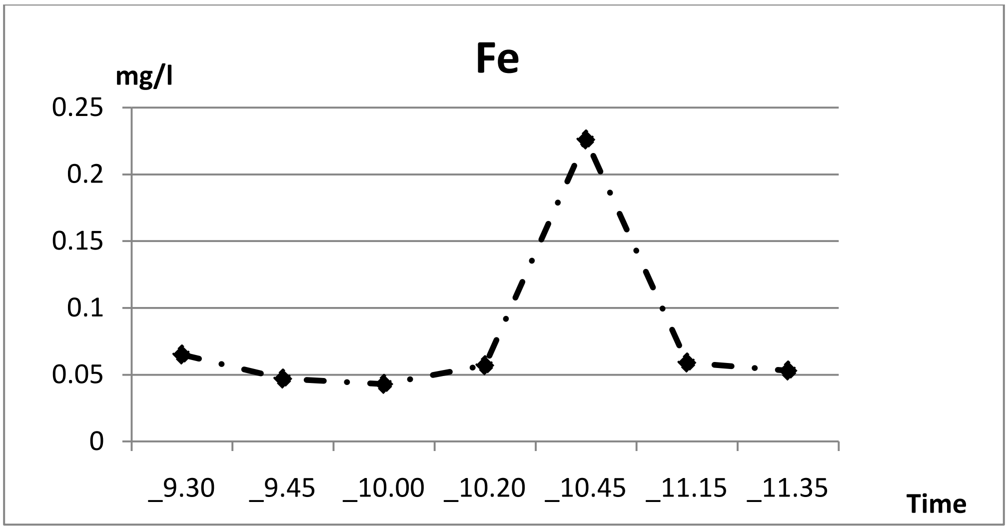


Fig. 6.10 TSS and total metal concentrations flowing into the lagoon

The correlation with TSS follows the sequence Fe > Zn > Cu.

Fig. 6.11 represents the same event but in terms of dissolved metals which were not predictable in terms of their behaviour (with time, flow rate or solids). Dissolved copper and zinc attained their highest values at the same time (10.45 am) as dissolved iron, although the profile of their concentration increase is much smoother.

a)



b)

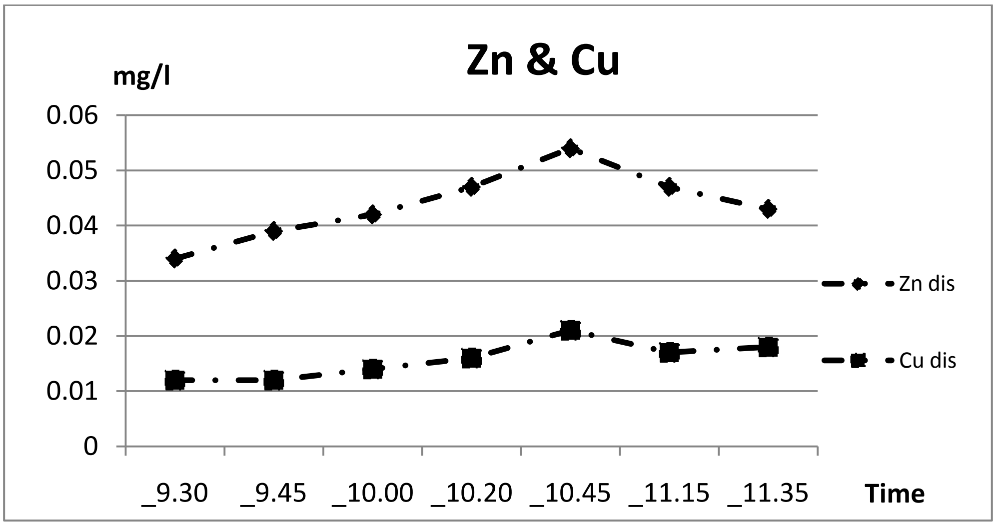


Fig. 6.11 Concentration of dissolved metals flowing into the lagoon

It was also apparent from this storm (Figure 6.10) that solid capture by the interceptor was not complete.

Interceptor performance monitoring

Interceptor performance was analysed on the basis of three observed rainfall events and samples were tested for PSD using the Mastersizer (see section 4.2.3). The events each had different characteristics and these are shown in Table 6.10.
The first storm in July (03/07/09), by contrast with those observed on the 11/07/08 and 09/09/08, followed a prolonged dry weather period. The actual discharge into the lagoon took place only after the interceptor had been refilled, which was after the rain had stopped (Table 6.10, 4th and 5th columns).

Photo 6.1 a shows the conditions in the inlet channel from the motorway junction prior to the storm event and Photo 6.1 b those during the storm event. Photo 6.1 c shows the ditch from the inlet channel to the interceptor (Photo 6.1 d). Photo 6.1 d shows the outlet from the separator and inlet into the lagoon during the storm itself. Photos 6.1 b, c and d were taken at the same time, from which it can be seen that the connecting channel before the interceptor was flooded, while the outlet and inlet to the lagoon were still dry with no discharge.

Water accumulation within the chambers of the interceptor from the beginning of the rainfall event till the beginning of the discharge (when the chamber was full) is shown in Fig. 6.12.

In contrast, the event observed in September (09/09/08) happened during an extended wet weather period and the rainfall pattern from the beginning of September till the sampling day is shown in Fig. 6.14. The separator was therefore already full (because of these overall weather conditions, the rain had already begun by the time sampling started). The total amount of rainfall in September 2008 up to 09/09/08 was 69.8 mm. In comparison, the amount of precipitation in September 2007 was 23.2 mm and in September 2009 it was 22.4 mm (see Appendix 1).

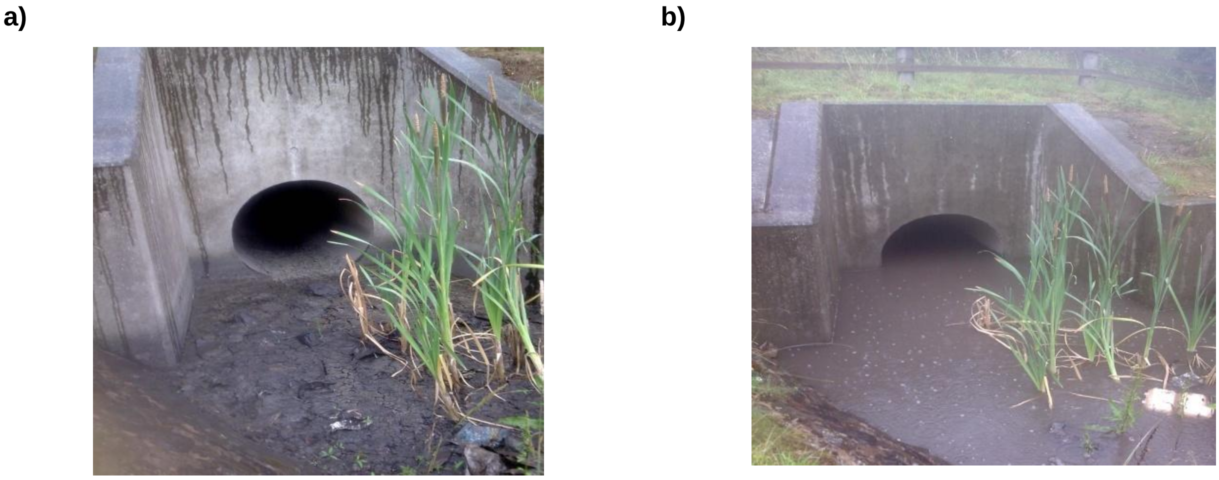
The discharge into the lagoon took place approximately 1.5 hrs after the rain had started (Table 6.10, columns 4 and 5$^{)}$, which confirmed that the water level in the

Table 6.10 Overall interceptor performance linked to some characteristics of the observed rainfall events

Date observed storm event	ADWP	Observed amount of precipitation, mm	Weather description	Time of taking samples for PSD and TSS concentration	TSS*
1	2	3	4	5	6
11/07/08	None (ground saturated)	**6** 12.50-13.50 – **4 mm** 14.00-14.20 – **2 mm**.	There were heavy and light showers throughout this week. There were 2 showers during the survey.	I – 2.50 pm;	42/7
				II – 3.00 pm	45/12
09/09/08	None (ground saturated)	**1.7** 9.30-9.45 – **1mm** 9.45-10.00 –few drops 10.00 – rain stopped 10.35 rain started again. 10.35-11.00 – drizzle (few drops) 11-11.15 – **0.5 mm** 11.15-11.25 – **0.2 mm**	Rain started approx. at 8 am. Rain gauge was installed upon arrival in the lagoon at 9.30 am.	I – 9.30 am;	13.75/4.75
				II – 9.45 am;	45/10.25
				III – 10.00 am;	76.43/22.5
				IV – 10.20 am	105.95/41
03/07/09	1 day**	**14.1** **time** **mm** **8.44** **9.00** **0.5** **9.15** **1.9** **9.30** **2.9** **9.45** **4.0** **10.00** **5.0** **10.15** **6.0** **10.30** **6.5** **10.45** **7.0** **11.00** **7.5** **11.15** **8.0** **11.30** **9.0** **11.45** **9.1** **12.45 b/w'=57** **Started again** **12.55** **13.10** **12** **13.25** **14** **13.40 Wind b/w'=70** **14.1**	Period of dry weather with very high temperature (~30). Inlet into the lagoon was dry. The water depth in the chamber of the interceptor was 48 cm	I – 2.00 pm;	86/10.5
				II – 2.15 pm;	118/49
				III – 2.30 pm.	121/41

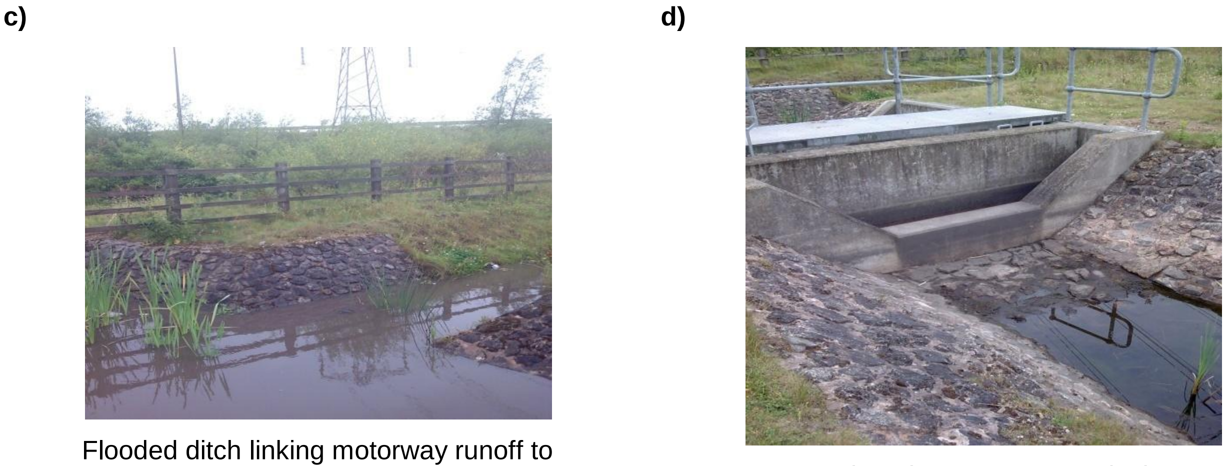
* Inlet of interceptor/ outlet of interceptor

** The amount of precipitation was negligible (0.2 mm on 01/07/2009 [see Fig.6.13]). Taking into account high ambient temperature, it was assumed that the rainfall did not produce runoff.



Inlet prior to the storm

Inlet during the storm



Flooded ditch linking motorway runoff to the inlet to the separator was flooded

Inlet into the lagoon was still dry

Photo 6.1 Rainfall event on the 03/07/2009 after a prolonged dry period, showing the moment when the area before the interceptor was flooded but not after it.

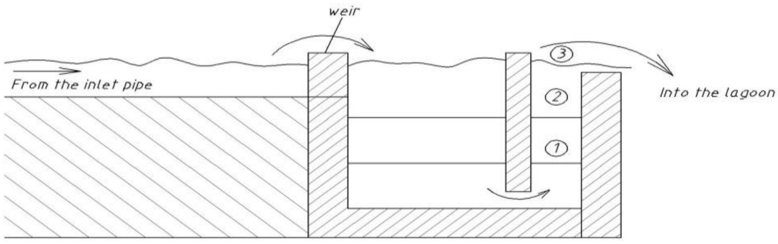


Fig. 6.12 Water accumulation within the interceptor.

① - prior to storm (48 cm); ② - 4 hours after the storm started (57 cm); ③ - overflowing point (70 cm) system (interceptor) was already high. Precipitations for the month and the event (09/09/08) which was observed within the wet weather period are shown in Fig. 6.14.

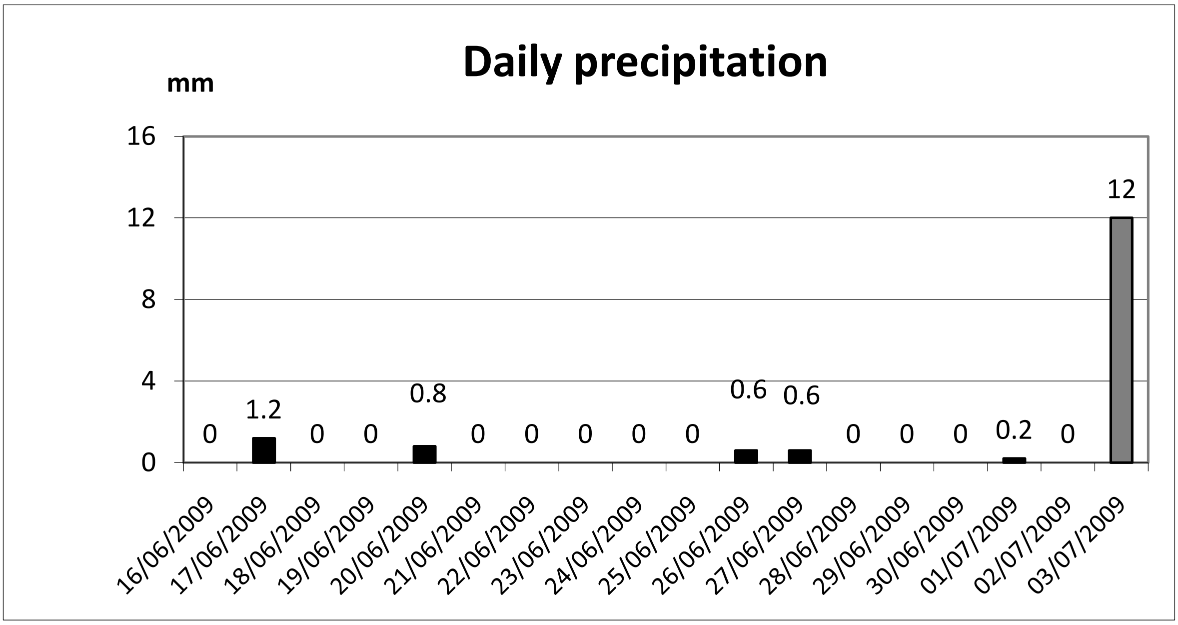


Fig. 6.13 Summer precipitation from 16th of June to 03rd of July 2009

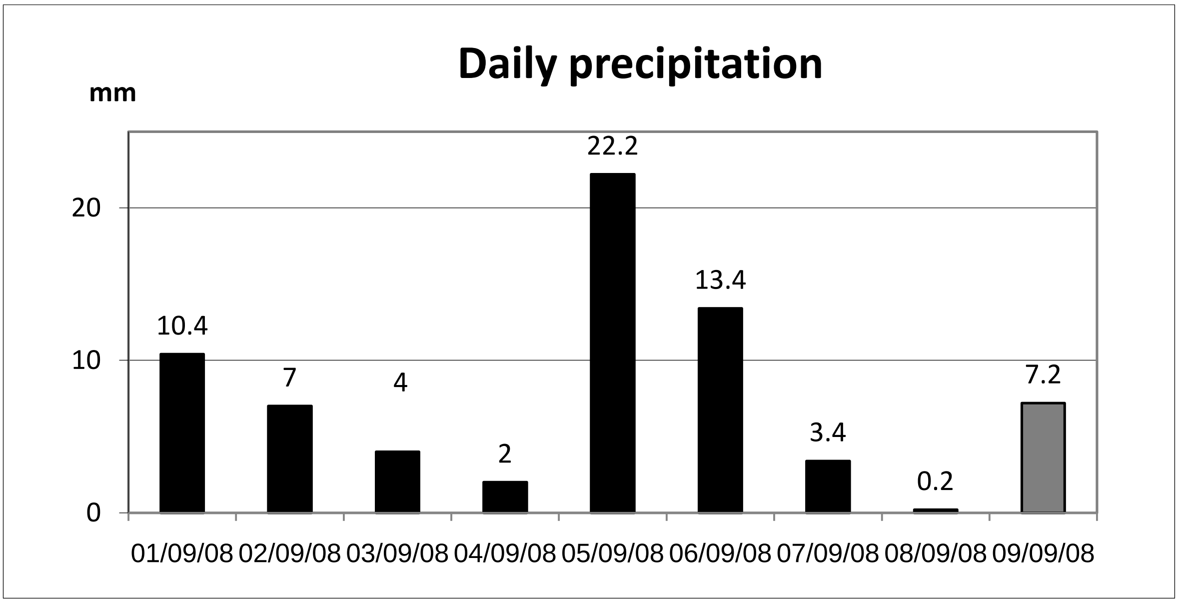


Fig. 6.14 Daily precipitation from 1st September to 9th of September 2008

The rain observed on 11/07/08 also happened during prolonged wet weather. Fig. 6.15 shows the rainfall pattern from the beginning of July till the observed rain event. Unfortunately, the samples for PSD were taken after the rain had stopped, although the discharge from the interceptor would have started long before the sample was taken, bearing in mind the wet conditions during that period.

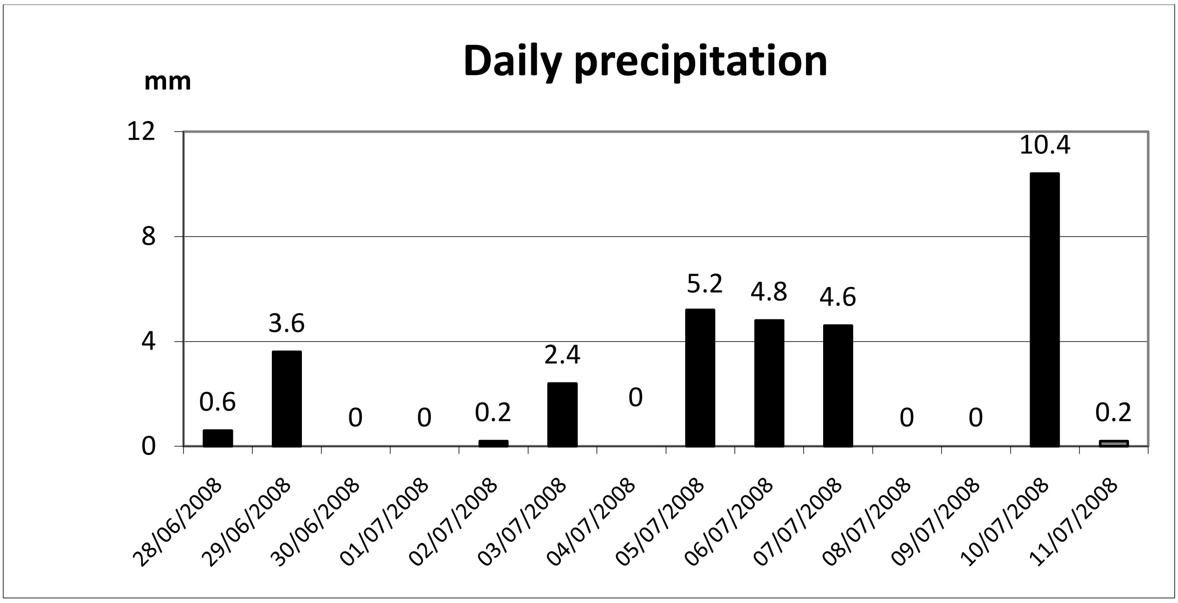


Fig. 6.15 Summer precipitation from 28th of June to 11th of July 2008

It should be noted that the amount of precipitation observed by us on that day (on the 11th July 2008; Table 6.10) (6 mm) was different from the official weather station at Leicester, where only 0.2 mm was recorded (see Appendix 1 and http://www.stormtrack.co.uk/ for details).

PSD analysis

These three storm events representing two dry periods in July and a wet month, September, were analysed in some more detail with regard to PSD and solid removal performance by the interceptor.

The particle size distribution in and out of the separator is shown in Figures 6.16 – 6.19 for the three detailed events. A shift to the left suggests a reduction in particle size, as might be expected if the interceptor selectively removes the larger particles.

Thus, for example, looking at the September 2008 storm first (an extended period of wet weather, see Fig. 6.14) the PSD noted at 9.30 am (Fig. 6.16 a) is as would

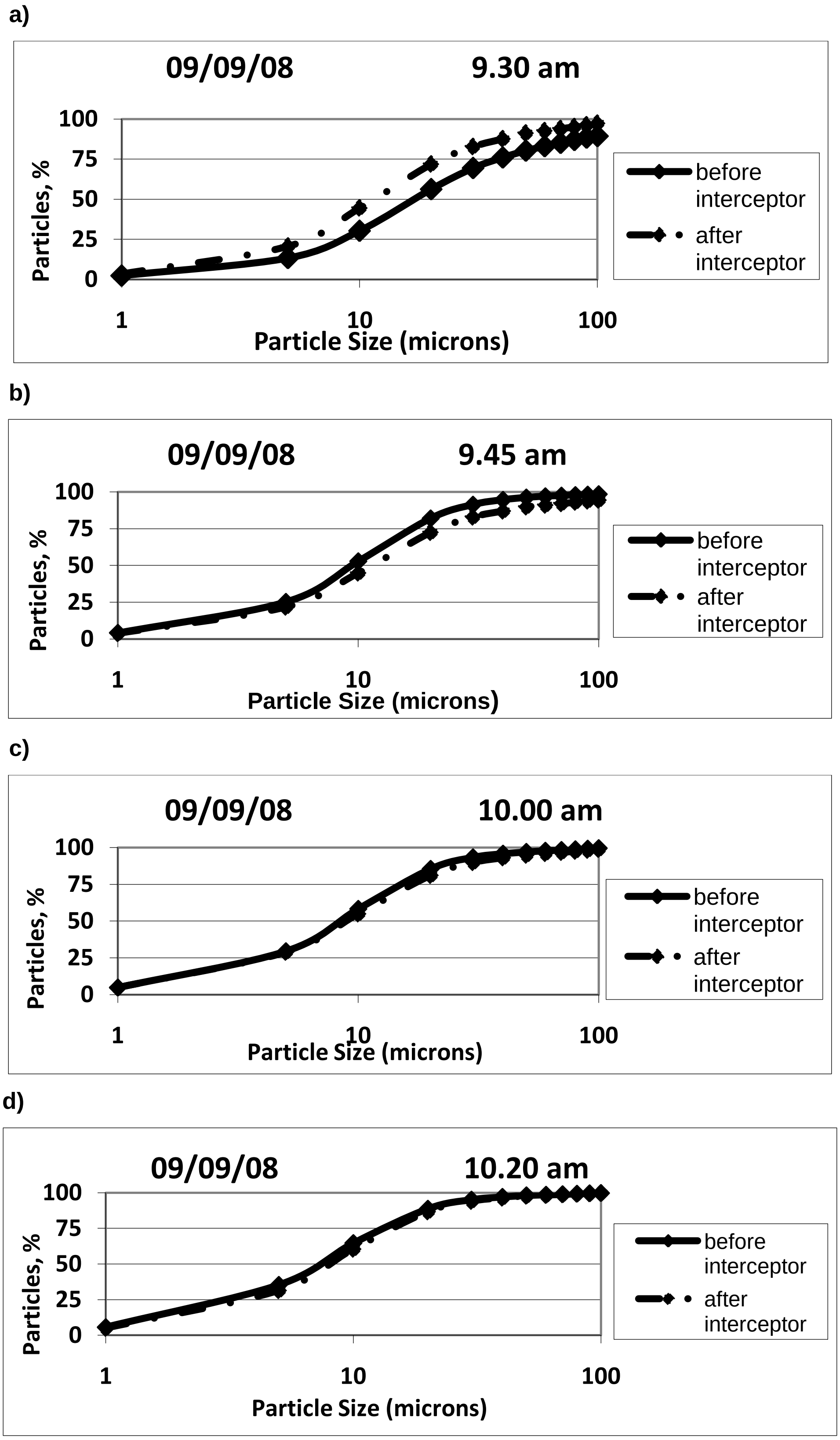


Fig. 6.16 PSD of the rainfall event on 09th of September 2008

be expected. There is a shift in particle size to the smaller sizes from the inlet to the outlet and this is because the larger particles are retained by the separator (TSS removal is 66%, Table 6.10).

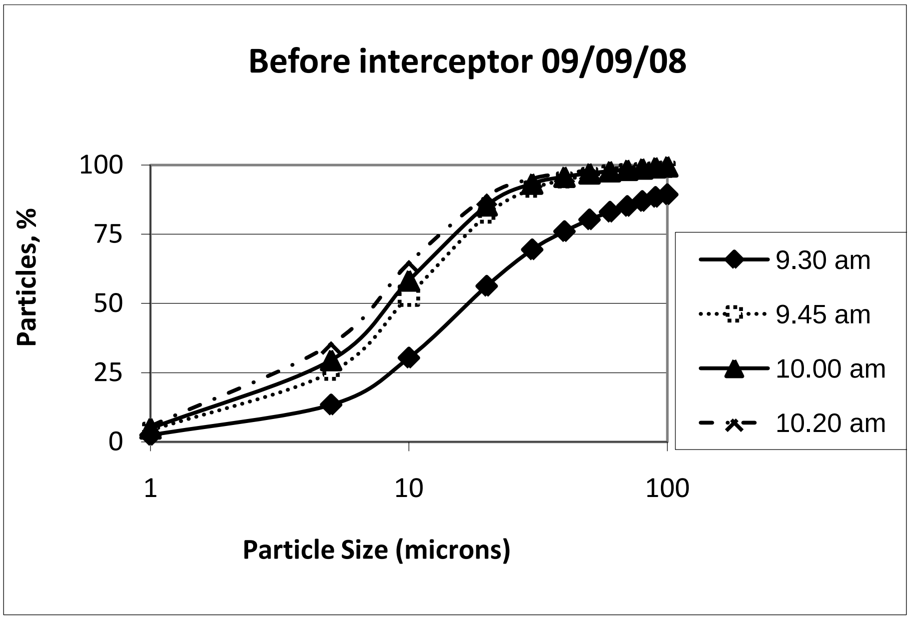
At 9.30 am the median particle size of the effluent (d_{50}) (after the interceptor) is 11.5 μm compared to that found at the inlet (d_{50}) (before the interceptor) of 17 μm. 15 minutes later, however, the pattern has changed (Fig. 6.16 b): the median particle size in the outlet is ~ 11 μm, as before, but the inlet median particle size has fallen to 9.5 μm, presumably due to dilution. The TSS in the feed and outlet from the interceptor increase during the storm (Table 6.10) and the solid removal efficiency also decreases, as might be expected as the PSD in the feed gets smaller.

The Mastersizer (see section 4.2.3) adjusts the PSD to the total volume of particles it analyses, so the reduction in particle size in the feed (Fig. 6.16) must therefore be combined with the increase in the number of particles to give a greater mass of TSS (Table 6.10).

The study of these three storm events pre-dates the purchase of the flow meter (see section 4.1.1) which would therefore have confirmed the greater flow and number of particles. The retention time of the separator may be estimated from the water level at the start of the storm (ADWP causing evaporation) and the time to overflow.

Analysing the readings from the flow meter recordings (see Appendix 3), it can be seen that the max retention time is 28 min at Q_{min} 6 l/s and the min. retention time is 5 min at Q_{max} 36 l/s (with the volume of the chamber being 10.5 m^3). Referring back to Table 2.7, this means that inorganic particles greater than 100 μm in size should be removed by the separator. Therefore, the suggested interpretation of this data is that it is dilution which causes the reduction in particle size but the increase in flow mobilises a greater concentration as the storm progresses. Larger particles of sediment are present in the initial stages of the storm but these are captured by the separator down to a critical particle size (~10 μm). Thus the data is evidence of first flush effects. This is summarised in Fig. 6.17 a and b which shows after the first sample 9.30 am at the start of the storm that the PSDs are all very similar.

a)



b)

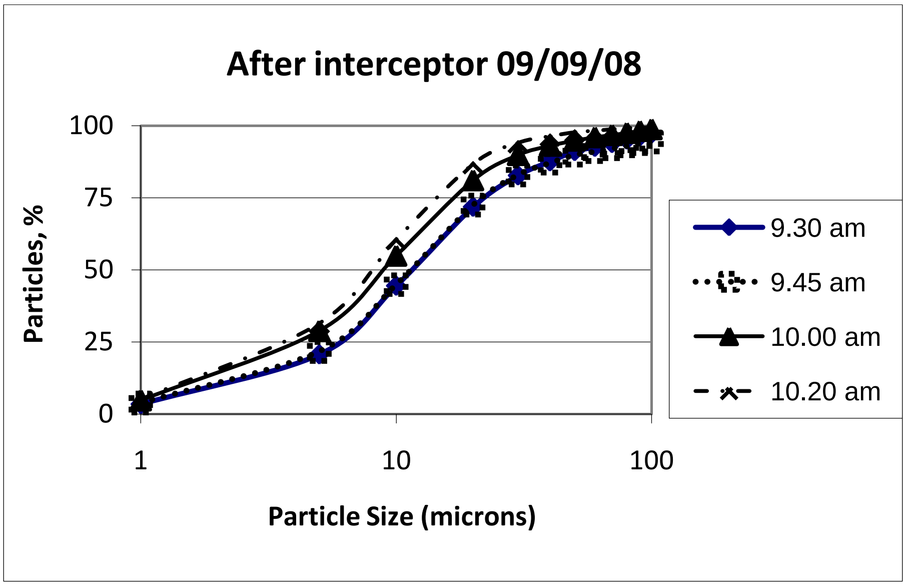


Fig. 6.17 Comparison of PSD before and after interceptor on 09th of September 2008

The TSS increased in both the inlet and outlet of the separator during the storm (Table 6.10), while the removal efficiency (range 60 – 70%) also decreased, as would be expected. As the flow rate increases the PSD reduces and this is the same in the inlet and outlet.

The ADWP effect on PSD should be magnified in the storm event investigated on the 3rd July 2009 since this occurred after a 17-day dry period. In this case the average particle size (d_{50}) in the feed (Fig. 6.18 a) is smaller than those in the

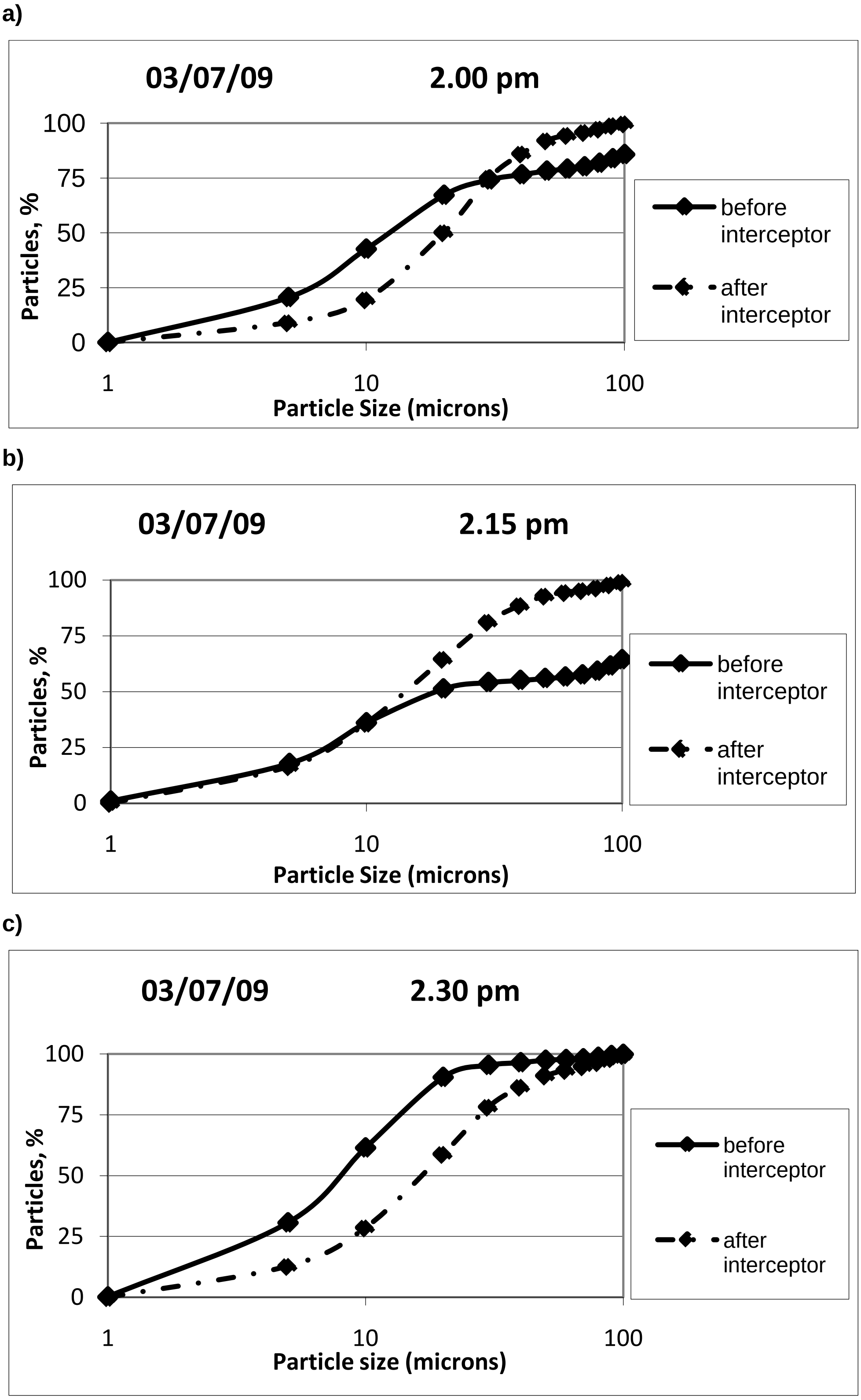


Fig. 6.18 PSD of the rainfall event on 03rd of July 2009

outlet, which must reflect the extended holdup time in the interceptor between inlet and outlet. The inlet flow in this storm does include some larger particles (> 100 um) of $d_{90,}$ as predicted from the 1st example storm because of the longer ADWP and, as suggested from Table 2.7, these were effectively removed by the interceptor.

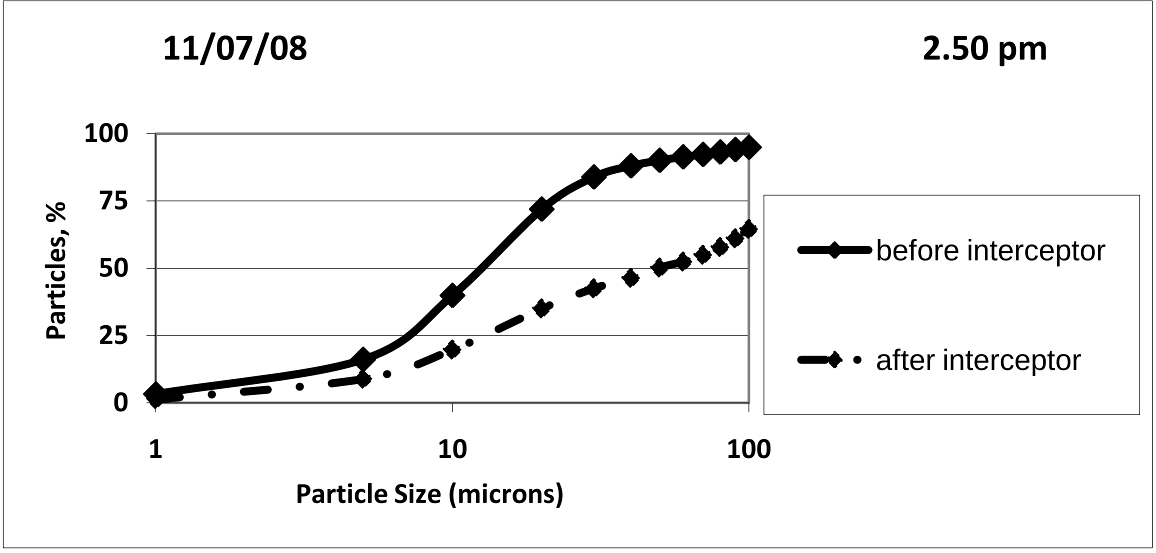
The TSS concentration in the inlet (at 2.15 pm [Table 6.10]) is greater than in the first sample, as would be predicted from the previous literature and results on ADWP. The TSS concentrations increased in both the inlet and outlet, as in previous storms, suggesting an increase in both particle numbers and flow rate. By the end of the storm (Fig. 6.18 c), then, most of the larger particles had been flushed through and captured by the interceptor. Although the particle size profile in the effluent is larger than in the inlet, this can again be attributed to the hold-up time in the interceptor. The PSD in the effluent is constant throughout the storm as in the first example storm, showing that the interceptor is successful in removing all the particles over the critical size (10 – 30 µm), but the increases in the number of particles at or below this size are indicative of an increase in TSS in the treated flow (Table 6.10).

The third example storm of 11th July 2008 was selected as a typical or average rainfall event (20 mm for the month) and the rainfall on the previous day gave a comparison between above-average and typical ADWP. The particle size profile in both the separated effluent samples was larger than that in the influent (Fig. 6.19). The PSD in both the treated samples were therefore also larger than in the previous storms. The rainfall was low but it followed a preceding wet day which, as suggested previously, had led to dilution and flush through of the larger particles.

The TSS removal during this case study storm were similar to those predicted (Table 6.10) by previous measurements, that is between 70 – 80% which were typical of the particle settlement velocity and retention time in the separator.

Table 6.11 summarises PSD for the three rainfall events of 10, 50 and 90 µm respectively. This data suggests that most of the particles had sizes of less than

a)



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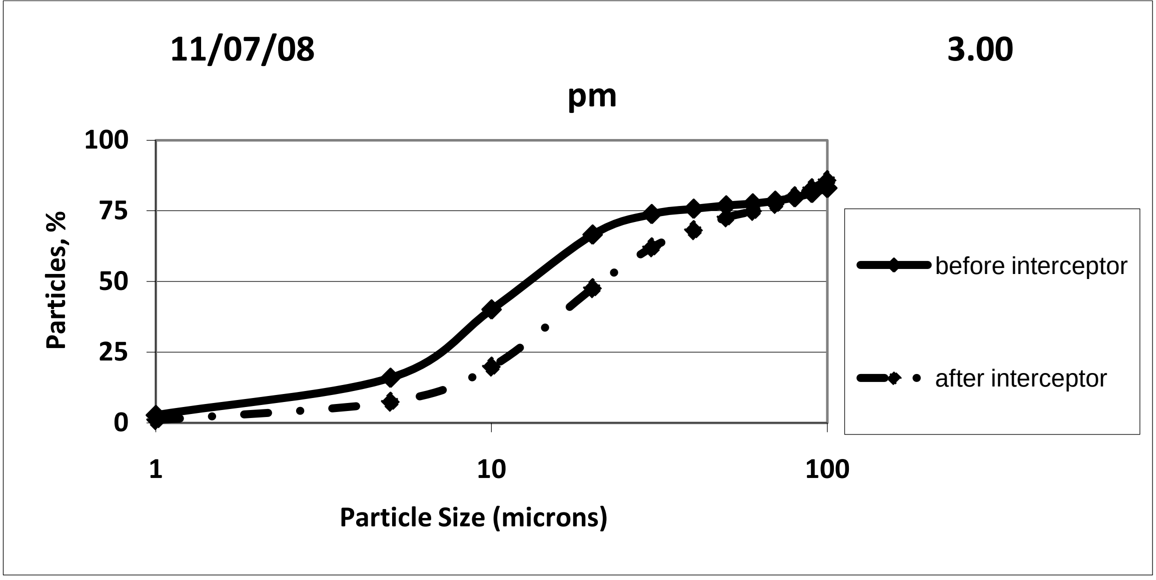


Fig. 6.19 PSD of the rainfall event on 11th of July 2008

100 µm. Given the size of the interceptor (10.5 m^3), most of the particles (< 50µm) would be expected to be removed and this was the case except for the storm event observed on 11/07/2008. The storm on 11/07/2008 produced a typical 6 mm of rain and, therefore, a possible explanation is that at this point in the storm particles were being re-suspended or were floating within the separator. More work is needed to gain a better understanding of particle size distribution based on their settling properties.

Table 6.11 Percentile of particles smaller than 10; 50 and 90 μm for three rainfall events

Time of sampling	Before interceptor			After interceptor		
	10	50	90	10	50	90
	11/07/08					
2.50 pm	39.9	90.13	94.13	19.74	49.51	55.82
3.00 pm	40.06	76.86	81.25	19.82	71.85	82.5
03/07/09						
2.00 pm	42.66	78.23	83.52	19.64	92.13	98.82
2.15 pm	36.04	55.89	61.48	35.95	92.94	97.89
2.30 pm	61.45	97.47	98.10	28.71	91.16	98.3
09/09/08						
9.30 am	30.31	80.27	88.51	44.45	90.59	96.1
9.45 am	52.84	96.25	98.15	44.89	89.36	93.68
10.00 am	58.28	96.97	99.92	54.95	94.84	98.09
10.20 am	64.6	97.93	99.46	60.49	97.52	99.48

Fig. 6.20 and Table 6.12 show another set of PSD but only in the inlet, where they were taken on 21/11/09 during prolonged wet weather. This event was not put together with others for comparison because the discharge into the lagoon was not analysed and only data taken before the interceptor was available. Another reason for its exclusion from the direct comparison was the availability of flow rate velocity data which enabled us to calculate the actual HRT.

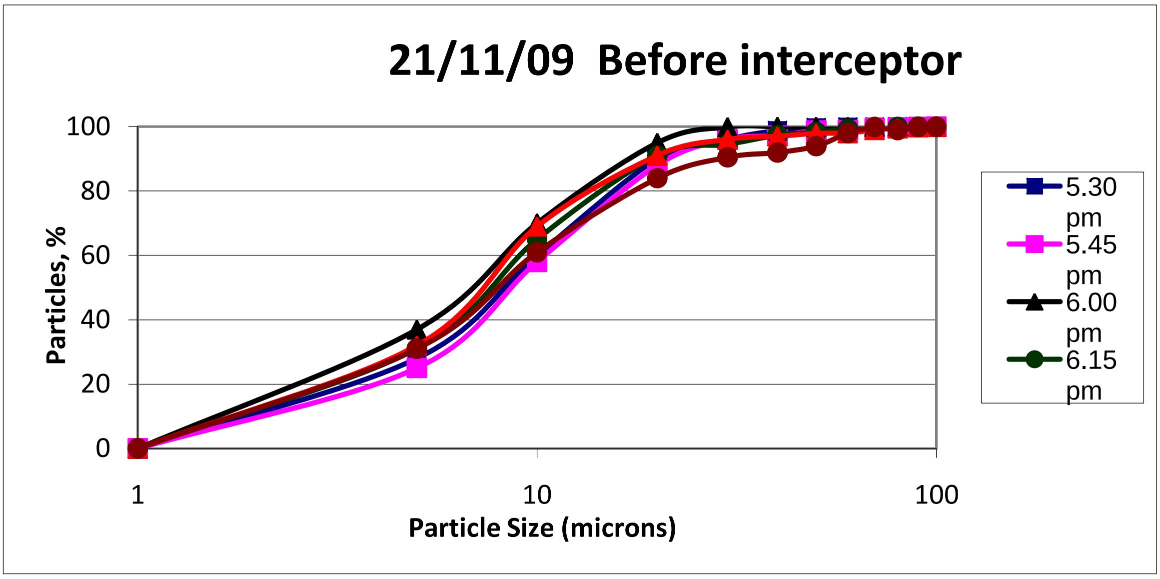


Fig. 6.20 PSD of the rainfall event on 21st of November 2009

Table 6.12 Percentile of particles smaller than 10; 50 and 90 µm for 21/11/09 rainfall event

Time of sampling	Before interceptor (Inlet)		
	10	50	90
5.30 pm	60.0	99.78	100.0
5.45 pm	58.01	98.85	99.9
6.00 pm	70.11	100.0	100.0
6.15 pm	65.04	98.31	100.0
6.30 pm	69.45	97.92	99.95
6.45 pm	61.25	94.34	99.94

In this case the feed median particle size was 9 µm which was typical of the previous wet weather. The retention time was calculated accurately as being 28 minutes, which should have removed all particles of more than 50 µm, assuming an SG of 2.5.

Thus, in conclusion the separator successfully removes on average 70 % of the TSS and almost all particles above 50 µm in size and therefore it provides protection or a reduction in solid load entering the lagoon, which is more difficult to maintain.

These measurements and observations made on site suggested an increase in turbidity in the separated runoff and sludge accumulation in the separator. As far as is known, with the site having been monitored for 15 years, the separator has not been discharged and the sludge depth was 8 cm or 20% of the available depth.

Soluble metals

Fig. 6.21 compares the concentrations of soluble/totals for the indicator metals in the treatment system for 7 observed rainfall events together with TSS and TOC as potential solids and dissolved mobilising ligands. TSS concentrations are again included before and after the interceptor to observe potential links between total metals and solid size (Fig. 6.21 a, c, e). From the analysis of the mean values in Fig. 6.21 a, c, e it can be seen that in most cases the interceptor removed TSS as well as total metals (see Table 6.10). The data from two storm events (13/11/2009

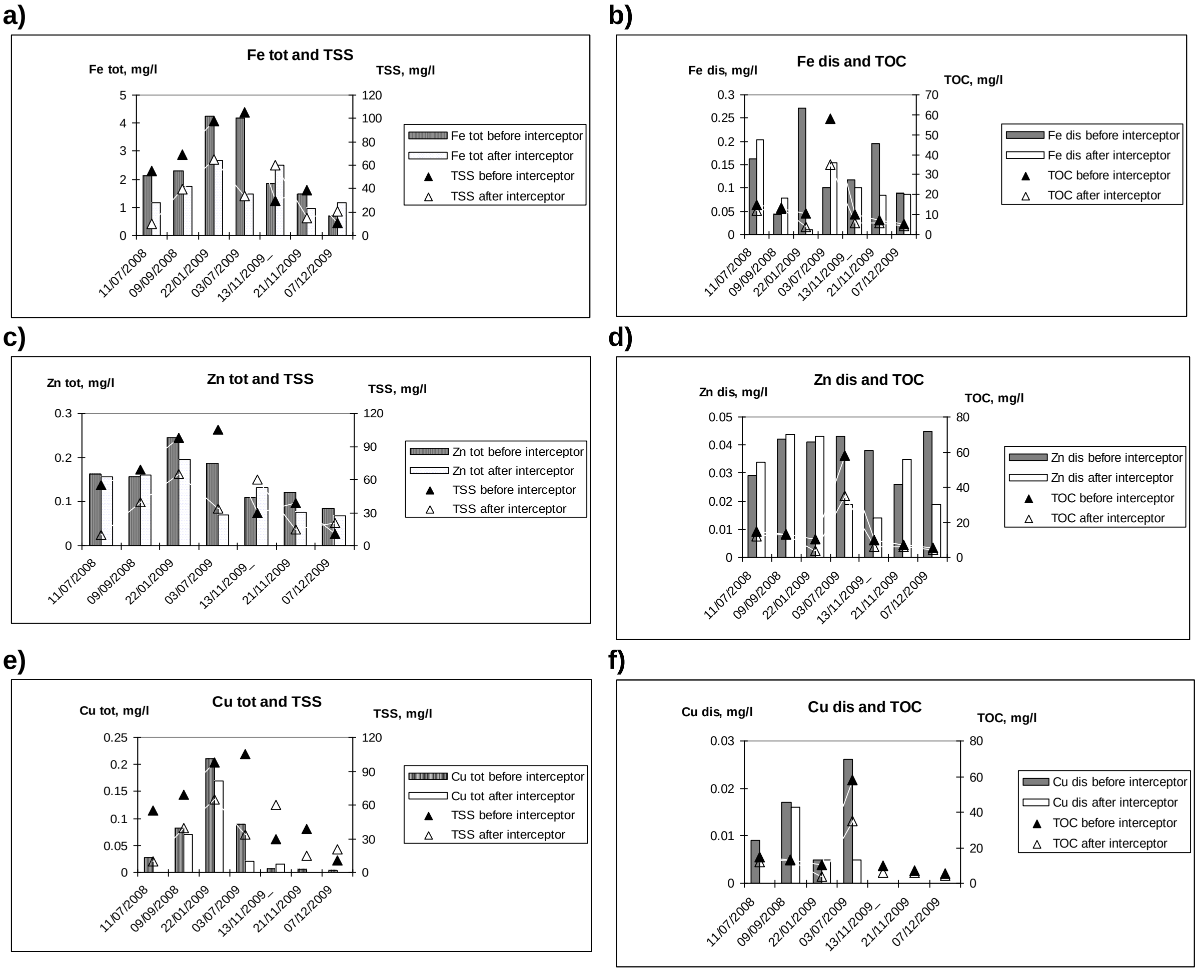


Fig. 6.21 Total and dissolved metals with TSS and TOC before and after interceptor during wet weather

and 07/12/09) showed that solid separation by the interceptor could be compromised by types of rainfall event and sampling when TSS were greater in the outlet of the interceptor. On the 13/11/09 (when the runoff duration was 390 min. with a peak flow of 31.93 l/s; see Appendix 3) the amount of precipitation noted from the nearest weather station was 4.0 mm (see Appendix 1) and only the “tail” of the rainfall event was sampled. At this point in the storm cycle the influent to the interceptor was highly diluted compared to the effluent because of the long storm and retention time or sediment was re-suspended from the bottom of the chamber. As has already been mentioned, the second rainfall event observed on 07/12/2009 happened during an extremely wet period with great dilution in the system and the TSS in the feed to the interceptor were the lowest recorded.

Fig. 6.21 b, d, f show the dissolved metals for these three observed rainfall events together with TOC as a potential soluble indicator of binding agents which could correlate with soluble metals. The data show no evidence of a link between TOC and soluble metals. This stands in contrast to some previous work which has suggested that soluble metals are complexed with the dissolved organic matter (Prestes et al. 2006).

For example, Prestes et al. (2006) observed a relationship between dissolved Cu, Pb and Cd and the concentration of DOC (see section 2.7.2). The best correlation between metals and DOC was reported for Cu, confirming that the latter has the potential to form more ligands with organic carbon in its dissolved form. In our data there may be a trend between TOC and dissolved Cu (Fig. 6.21 f), but because the samples are taken from the free-flowing traffic the total copper concentrations are lower than those reported by Prestes et al. (2006). In urban areas the dissolved copper concentrations are reported to be in the range 0.01 – 0.025 mg/l (Mosley and Peake, 2001; Gnecco et al., 2005; Berretta et al., 2008) and in Fig. 18 f they peak at 0.022 mg/l.

Comparing Fig. 6.21 a, c, e with 6.21 b, d, f it can be seen that dissolved metals do not follow the simple solid separation pattern, which provides supporting evidence for the inference that these metals are truly dissolved.

One of the objectives of the research identified by the literature review and these data was to determine whether a stronger adsorption (charge) was needed to reach both the EQS and background concentration. All the samples taken in our study achieved the EQS but these data were from free-moving traffic. These experiments are described in section 6.6.

Table 6.13 compares the indicator metals in the treatment system for the M1 (all samples being wet and dry) with a similar treatment system for the M40 monitored by Crabtree et al. (2006). The results show that on average this recommended treatment system, composed of separator and lagoon (Highways Agency, 2006), achieved background concentrations of metals (see section 2.4).

Table 6.13 Comparison of pollutant removal

Sample points	Average concentrations and range of pollutants, mg/l									
	M1					M40/Souldern Brook**				
	Zn tot	Zn dis	Cu tot	Cu dis	TSS	Zn tot	Zn dis	Cu tot	Cu dis	TSS
Highway runoff	0.175	0.035	0.061	0.012	75.7	0.1	0.025	0.025	0.01	75
(range of 7 samples)*	0.127-0.312	0.025-0.048	0.014-0.167	0.005-0.042	22-179					
Runoff after the oil interceptor	0.175	0.044	0.084	0.012	47.1	0.09	0.012	0.02	0.01	75
(range of 30 samples)*	0.079-0.261	0.005-0.054	0.004-0.161	0.002-0.021	4.8-81					
Discharging to water body	0.048	0.020	0.016	0.004	11.6	0.04	0.006	0.008	0.005	25
(range of 22 samples)*	0.009-0.153	0.002-0.069	0.003-0.041	0.002-0.009	3.2-39.5					

* number of samples in brackets are related to the M1 only ** modified from Crabtree et al. 2006

The average concentrations of the metals from the M1 are higher (see Table 6.13) than those found at the M40 site, which can be explained by the greater traffic flow on the M1 (30,000 and 7,000 vehicles per hour, respectively). The TSS and range of metal concentrations are similar from both sites. Another possibility for explaining the difference could be the use of different analytical techniques (microwave digestion was used for the M1 samples; see method development section 4.2.2). There were also differences between the two sites with respect to the removal of suspended solids. During sampling visits to the M1 when there was intense prolonged rainfall it was perceptible, as discussed (see PSD section), that TSS were being re-suspended in the interceptor and this possibility is recognised by the inclusion of by-pass systems in the design guide (Highway Agency, 2006). Further work will be needed, however, to monitor and develop methods for identifying when interceptors need emptying. The results also indicate that the standard combination of interceptor and lagoon did not always achieve the current EQS for total Zn. The Zn standard is unusual since it is expressed as totals.

6.3 SEWAGE WORKS

Taking the mean values for all the sewage works, then the total Fe was always at the highest concentration (Table 6.14). For the dissolved metals the highest concentration was that of Fe for Shepshed and Osgathorpe, whereas Zn was the highest dissolved metal for Loughborough and Leicester. Copper, both in total and dissolved forms, had the highest concentration from Osgathorpe. As would be expected, all the metals apart from Fe and Cu at Leicester were found predominantly in the dissolved form. The percentage of soluble metals is displayed in Fig. 6.22.

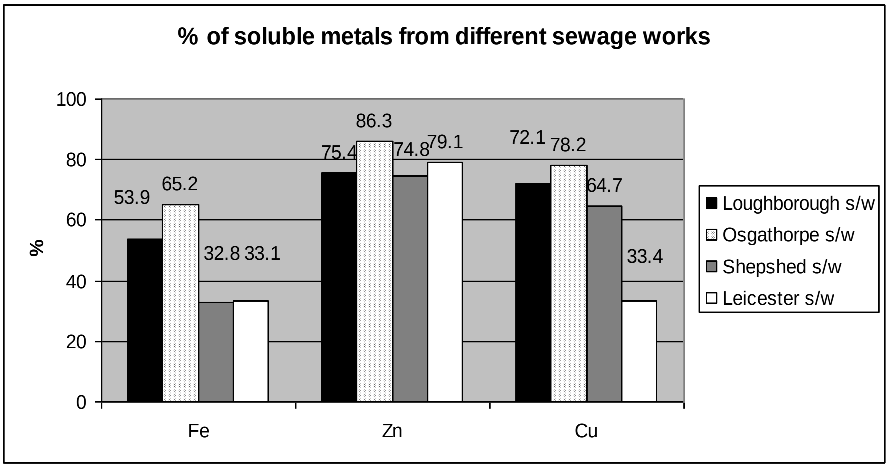


Fig. 6.22 Percentage of Fe, Zn and Cu from different sewage works

The percentage of soluble Zn is consistently high for all sewage works, indicating that most of the Zn was found in the dissolved from. The behaviour of Fe and Cu was more variable than that of zinc. The percentage of dissolved Cu found in Leicester sewage works was relatively small (33.4%), which could simply be related to the small number of samples. Copper obtained from the rest of the works was mainly in the dissolved form. The highway samples suggested a greater proportion of insoluble iron but at the sewage works most insoluble materials are removed (turbidity value is less than 2 NTU). The data from Leicester and Shepshed sewage works cannot be reliable because of the small number of samples taken (2 and 3 respectively).

Table 6.14 Data from the sewage works*

Contaminant, mg/l except turbidity and EC		Sewage works									
		Shepshed (3 samples)	Leicester (2 samples)	Loughborough (8 samples)				Osgathorpe (6 samples)			
		range	range	range	$\bar{X}$	S	C_v	range	$\bar{X}$	S	C_v
Fe	tot	0.073 – 0.23	0.109 – 0.139	0.047 – 0.082	0.060	0.012	0.202	0.108 – 0.126	0.118	0.008	0.066
	dis	0.034 – 0.049	0.038 – 0.044	0.026 – 0.039	0.033	0.004	0.112	0.059 – 0.094	0.077	0.015	0.196
Cu	tot	0.003 – 0.011	0.003 – 0.009	0.002 – 0.01	0.005	0.003	0.562	0.002 – 0.067	0.017	0.025	1.471
	dis	0.002 – 0.007	0.002	0.002 – 0.008	0.004	0.002	0.608	0.002 – 0.058	0.013	0.022	1.67
Zn	tot	0.032 – 0.049	0.079 – 0.093	0.039 – 0.069	0.060	0.015	0.250	0.025 – 0.081	0.054	0.020	0.365
	dis	0.024 - 0.031	0.064 – 0.072	0.029 – 0.07	0.051	0.017	0.323	0.018 – 0.065	0.046	0.017	0.358
TDS		410 - 480	550 - 680	460 – 550	490	39.37	0.081	370 – 570	447	68.61	0.153
pH		7.3 – 7.4	7.1 -7.2	7 – 7.5	7.26	0.23	0.032	7.2 – 7.4	7.3	0.089	0.012
EC, µS/cm		810 – 940	1080 - 1380	920 – 1140	996	88.49	0.089	800 - 1120	915	114.3	0.125
TOC		7.44 – 8.01	3.67 – 10.6	4.6 – 8.29	6.522	1.49	0.229	12.29 – 19.26	14.903	3.79	0.254
Hardness		210 – 280	235 - 325	235 – 425	309	78.93	0.255	185 – 280	238.3	48.563	0.204
TSS		8 – 15	11 - 14	8 – 11	9.4	1.517	0.161	10 – 20	14	4.54	0.324
Turbidity, NTU		1.56 – 2.05	1.52 – 3.16	0.733 – 1.77	1.26	0.405	0.321	2.53 – 4.76	3.45	0.869	0.252

*- total metals were recovered by hot plates

According to previous studies (Davis and McCuen, 2005) and our results for Fe in highway and urban runoff, Fe was predominantly insoluble. The concentration varied depending on the weather conditions**.** Data from these sewage works for Fe solubility (see Table 2.4) are different (Bubb and Lester, 1995), for example. A possible reason for the greater solubility of Fe in sewage work effluents could be the different types of organic matter present in sewage effluent compared to highway and urban runoff. Figs. 6.23 and 6.24 show potential links between organic matter (expressed in TOC) and solids (TSS) linked to soluble metals from Loughborough and Osgathorpe sewage works. They indicate that there is no evidence of a link between total organic matter, expressed by TOC, that would allow us to predict soluble metals. There are two potential reasons. Firstly, the range of TOC from Loughborough sewage works was from 4.6 to 8.29 mg/l, which is possibly too small compared to the highway and urban runoff for finding a good correlation. Another reason for the poor or even negative correlation is that a larger number of samples is needed to be statistically significant.

There was some support for this suggestion in the sewage work effluent too. The concentrations of Fe_{tot}, Cu_{tot} and Zn_{tot} were higher in the microwave digestion samples (Figure 6.25 d – f).

Another feature of the data is that there is no correlation between organic matter and TSS, which again can be explained by the small range of both TOC and TSS (Fig. 6.27).

Figs. 6.25 and 6.26 represent potential links between metals in their total forms and TSS. Evidence was sought from these Figures for the supposition that the method of analysis applied for metal recovery was an important factor in defining total metal concentrations, as was discussed in section 6.1.

Another aim of the sewage work study was to assess if sewage effluent affects metal concentration and their availability within the receiving water bodies. This was analysed with regard to the samples from Osgathorpe sewage works which discharges its treated effluent into the Grace Dieu Brook draining the National and Charnwood Forests.

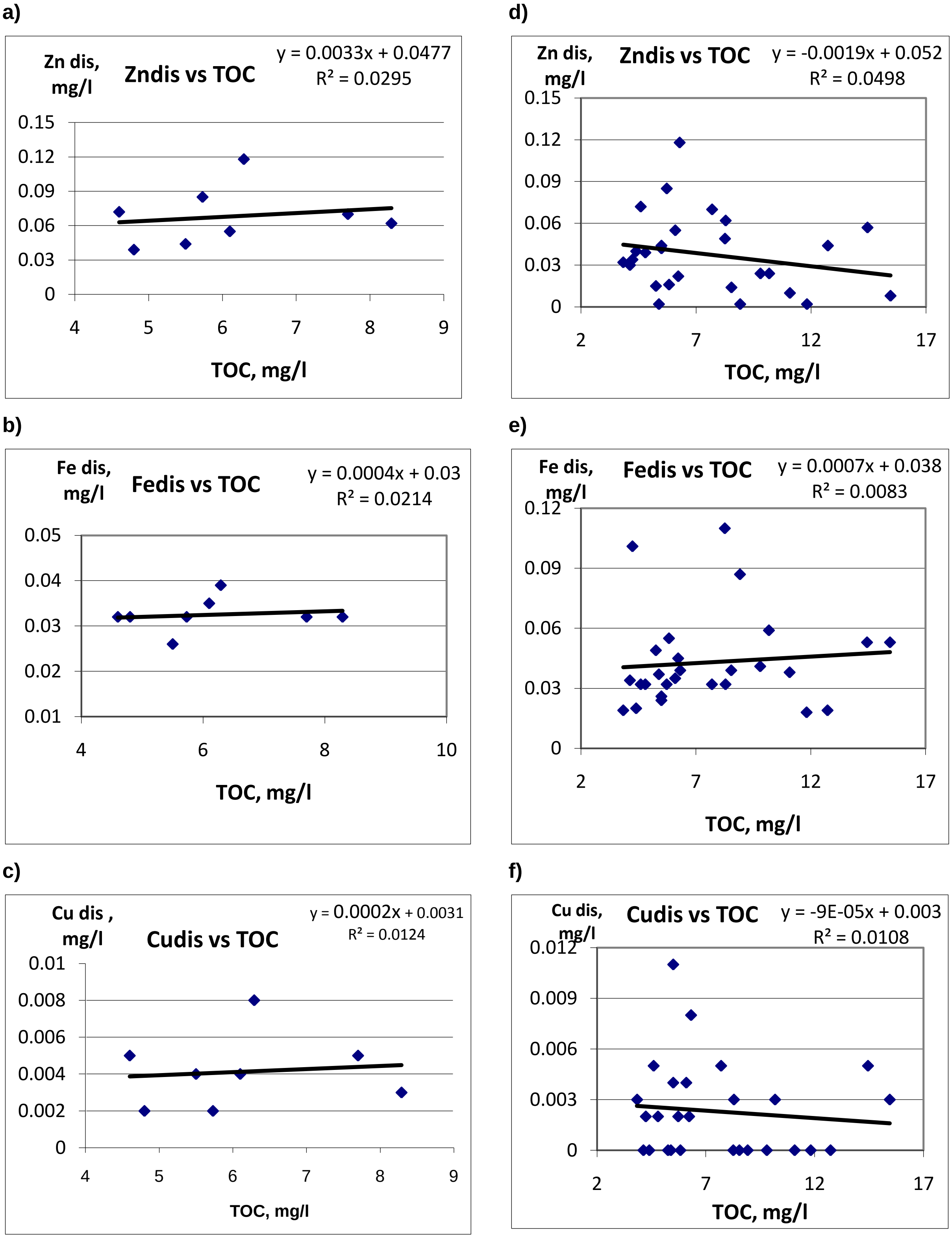


Fig. 6.23 Correlation between dissolved metals and TOC found from Loughborough sewage works. **a); b); c)** – hot plates – 8 samples; **d); e); f)** – microwave digestion – 19 samples

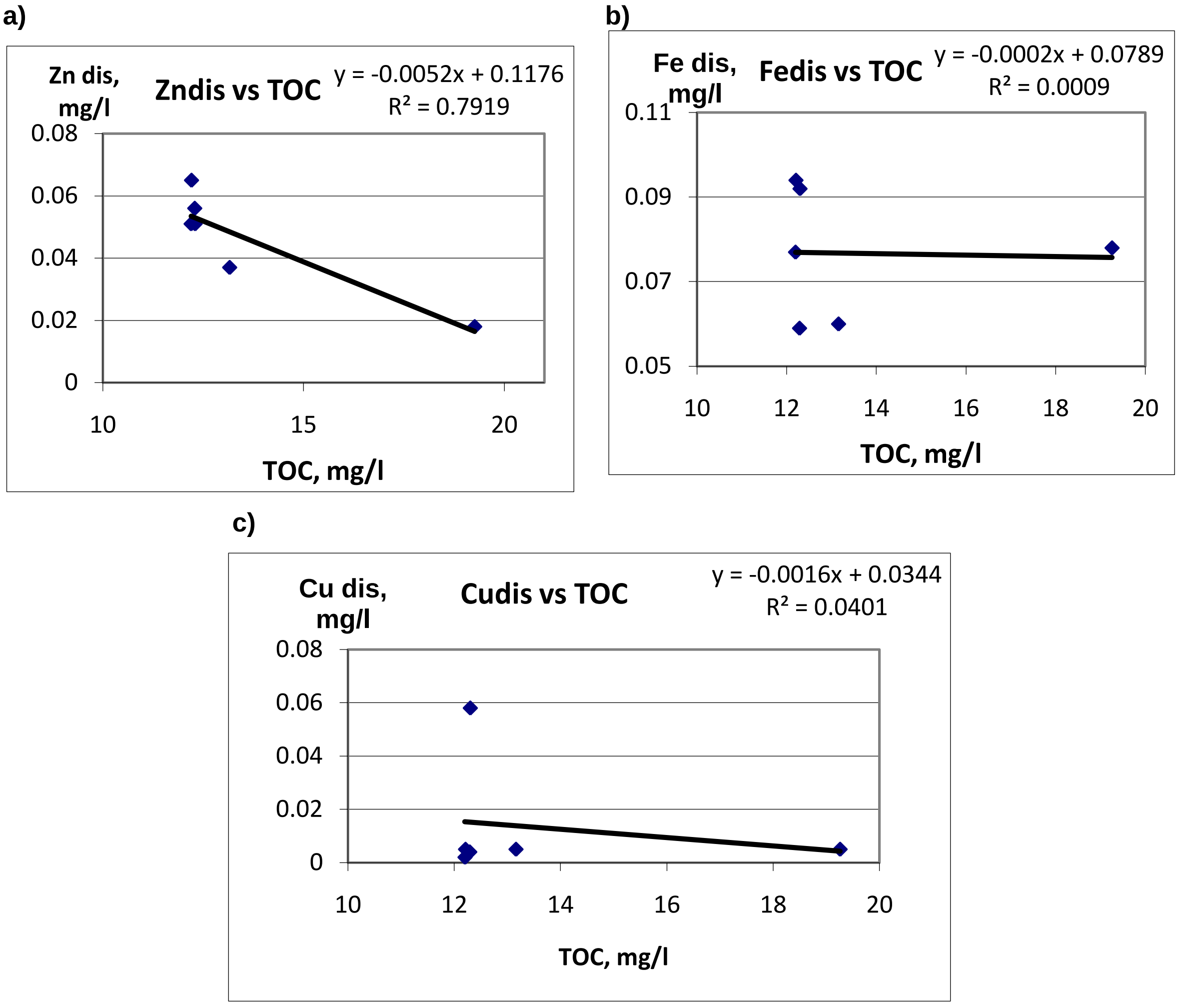


Fig. 6.24 Correlation between dissolved metals and TOC found from Osgathorpe sewage works

This was compared with research conducted by Bubb and Lester (1995) (see section 2.5), whose main interest was the effect of metals in sewage effluent on the receiving water. The data were also compared with the treated runoff from the M1 and Woodbrook.

The results from Bubb and Lester (1995) are presented in Table 6.15, while comparative data from our results are shown in Table 6.16. The shaded column (Table 6.16) represents the concentrations of metals and other water quality parameters calculated from the mass balance equation (Warn and Brew, 1980) used by Bubb and Lester (1995) for estimating river quality downstream of an effluent discharge:

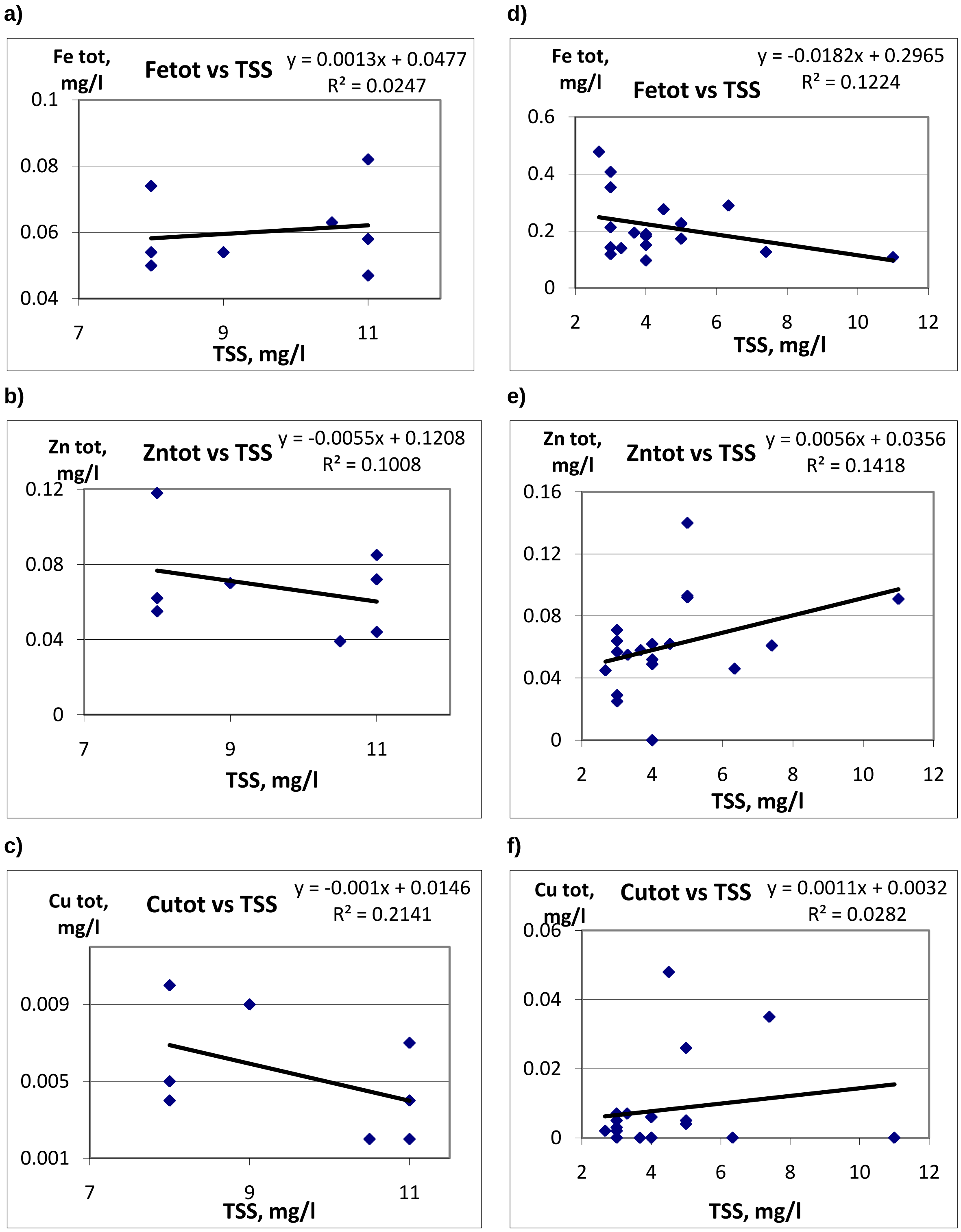


Fig. 6.25 Correlation between total metals and TSS found from Loughborough sewage works.
a); b); c) – hot plates – 8 samples; **d); e); f)** – microwave digestion – 19 samples

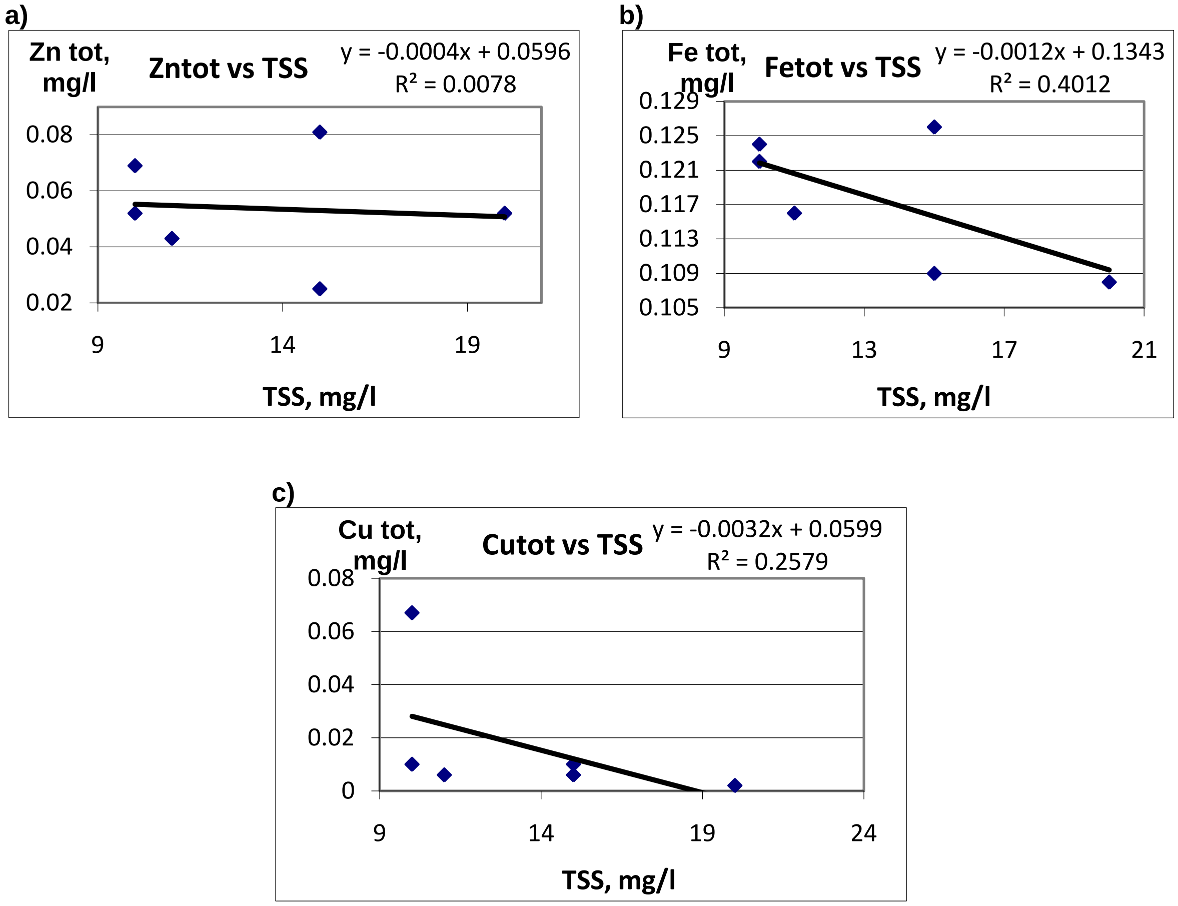


Fig. 6.26 Correlation between total metals and TSS found from Osgathorpe sewage works (hot plates)

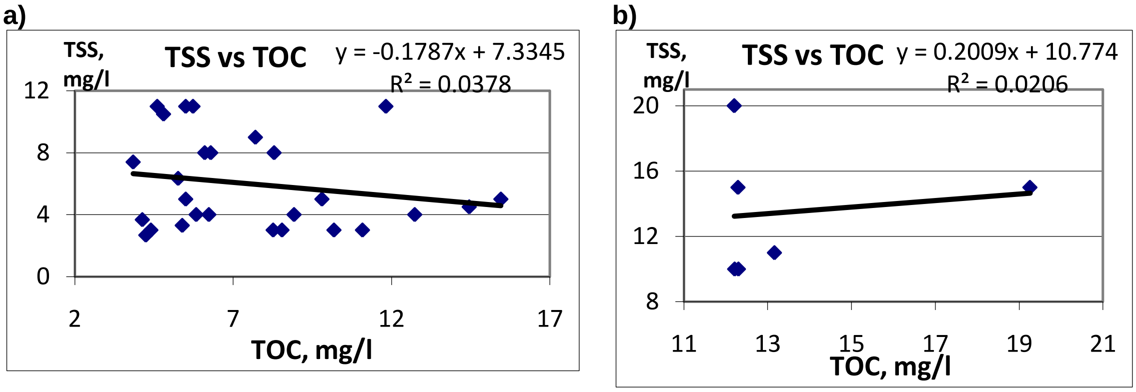


Fig. 6.27 Correlation between TOC and TSS found from **a)** Loughborough sewage works (27 samples) and **b)** Osgathorpe sewage works (6 samples)

$$C_{downstr} = \frac{(QC_{upstr} + qc)}{Q + q}, \qquad (6.3)$$

where $C_{downstr}$ - concentration of river water downstream of discharge; Q - river flow rate upstream; C_{upstr} - concentration of pollutants in river water upstream; q - flow rate effluent discharge; c - concentration of pollutants in the effluent discharge.

Our data reveal an increase in Cu and Zn loadings below the sewage works on the Grace Dieu Brook. This is not obvious in the Bubb and Lester analysis. The concentrations of Fe, both total and dissolved, decreased below the sewage work outfall in our study as a result of dilution by the sewage work effluent. Other parameters increase: TSS, for example, rises from 8.39 to 11.85 mg/l, TOC from 8.08 to 16.67 mg/l and NO_3 from 23.99 to 90.29 mg/l.

Table 6.15 Concentrations of some metals and water quality parameters in samples taken from Pix Brook and Letchworth Treatment Works*

Pollutant, mg/l, apart from pH	Upstream river water	Letchworth Treatment Works	Downstream river water	Predicted conc. below outfall**	Absolute error in model, %
TSS	1.1	4.2	6.7	3.66	45.3
TDS	443	688	627	645	2.8
TOC	2.3	7.85	7	6.9	1.43
pH	8	7.46	7.65	7.55	1.31
Hardness	288	286	273	286	4.5
NO_3 (N)	0.04	0.15	0.25	0.13	48.0
Fe_{tot}	0.06	0.06	0.293	0.06	59.0
Fe_{dis}	0.025	0.041	0.041	0.037	9.8
Cu_{tot}	0.00165	0.00173	0.00146	0.00145	0.68
Cu_{dis}	0.001	0.00146	0.00123	0.00123	0

* - modified from Bubb and Lester, 1995

** - using the equation of Warn and Brew, 1980

The results indicate that Zn, both in total and dissolved, and Fe_{dis} were the only metals that behaved according to the predictions of the mass hydraulic balance model.

The measured value of Fe_{tot} was 1.7 times higher than that predicted by the equation (6.3). This might be explained due to the bias from particulate matter re-suspended from the stream bed. The value for soluble Fe does agree well with the predicted value, which is understandable, bearing in mind that Fe has a poor solubility in water. The chosen sample point was immediately after the sewage work outfall and the surge in flow provoked turbulence, which resulted in the disturbance of particulate matter into suspension. Bubb and Lester (1995) reported the same fact in their study (see Table 6.15 for Fe_{tot} and TSS) and they attributed this to the channel morphology, which is therefore important in predictions of concentration.

Table 6.16 Concentrations of some metals and water quality parameters in samples taken from Grace Dieu Brook

Pollutant, mg/l, apart from Turbidity; EC and pH	Grace Dieu Upstream of outfall	Osgathorpe Treatment Works	Grace Dieu Downstream of outfall	Predicted conc. below outfall*	Absolute error, %
TSS	8.39	14	11.85	13.17	11.1
Turbidity, NTU	5.09	3.45	4.83	3.69	23.6
EC, µS/cm	640	915	905	875	3.3
TDS	320	445	452	430	4.9
TOC	8.08	14.9	16.67	13.89	16.7
pH	7.46	7.3	7.28	7.32	0.5
Hardness	210	238	210	233	10.9
NO_3	23.99	106.72	90.29	94.79	4.7
Fe_{tot}	0.28	0.118	0.248	0.142	42.7
Fe_{dis}	0.119	0.077	0.079	0.083	5.06
Cu_{tot}	0.006	0.017	0.008	0.015	87.5
Cu_{dis}	0.003	0.013	0.005	0.012	140
Zn_{tot}	0.026	0.054	0.056	0.049	14.3
Zn_{dis}	0.018	0.046	0.048	0.042	9.5

Q = 20 l/s; q = 10,000 m^3/day

* - using the equation of Warn and Brew, 1980

The behaviour of Cu (both soluble and total) was erratic, with differences between the measured and predicted values. Concentrations of Cu_{tot} and Cu_{dis} were much less than those predicted, thereby demonstrating that the behaviour of Cu was complex, as noted earlier (see section M1, dry and wet). Bubb and Lester (1995) suggested that the discrepancy for metals was likely to be 20 – 30% because of the crude nature of the mass calculations and average flow conditions. In their study the dilution ratio was calculated from dissolved chloride and it was suggested that sewage works contributed 82.6% of the Pix Brook flow downstream. Our sewage works make a lower contribution to the Grace Dieu Brook. The partitioning of Cu and Zn changed below the Osgathorpe sewage works. It is noticeable that the proportion of soluble Zn increased from 71.6% to 85.4%, which suggests an effect of organic matter, temperature or household products with solubilised zinc. The percentage of soluble copper also increased from 55.7 to 66.7%.

The discharge of sewage effluent changed the chemical composition of the Grace Dieu Brook. Enrichments were evident in EC, TDS and TOC. There was a significant increase in NO_3 after the sewage work outfall. This is mainly a trickling filter works which has only recently been modified to denitrify. The mass balance calculations showed that most of the water quality parameters (EC, TDS, pH, hardness, NO_3, TSS, turbidity) behaved conservatively.

The data obtained from Grace Dieu Brook before and after the sewage outfall during dry and wet weather are compared in Figures 6.28 and 6.29 (9 dry weather and 3 wet weather samples). From Fig. 6.28 the results show that for dry weather there is an increase in the concentration of all metals due to the sewage outfall (as Table 6.16). During wet weather the quality and quantity of flow from the sewage works is a smaller proportion of the total flow in the brook. Consequently there is a

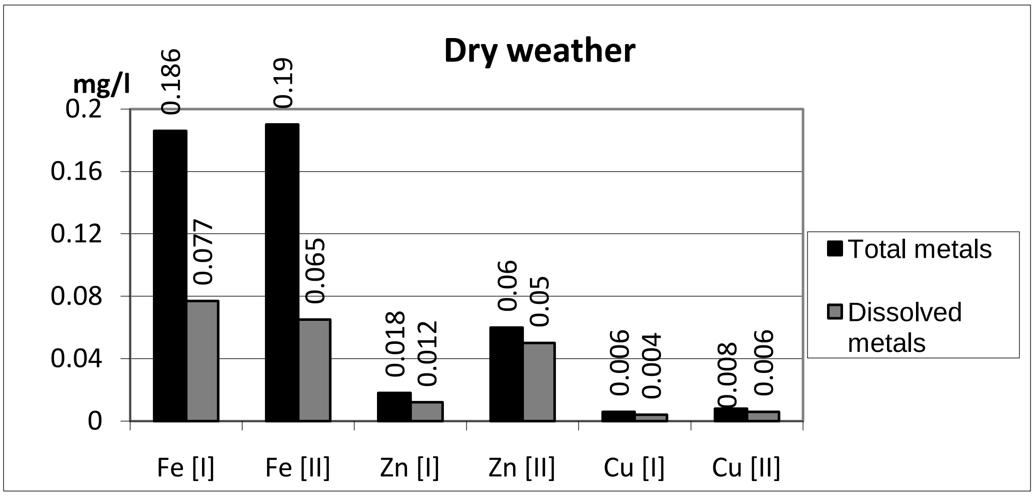


Fig. 6.28 The mean value of metals during dry weather: I – before sewage outfall; II – after sewage outfall

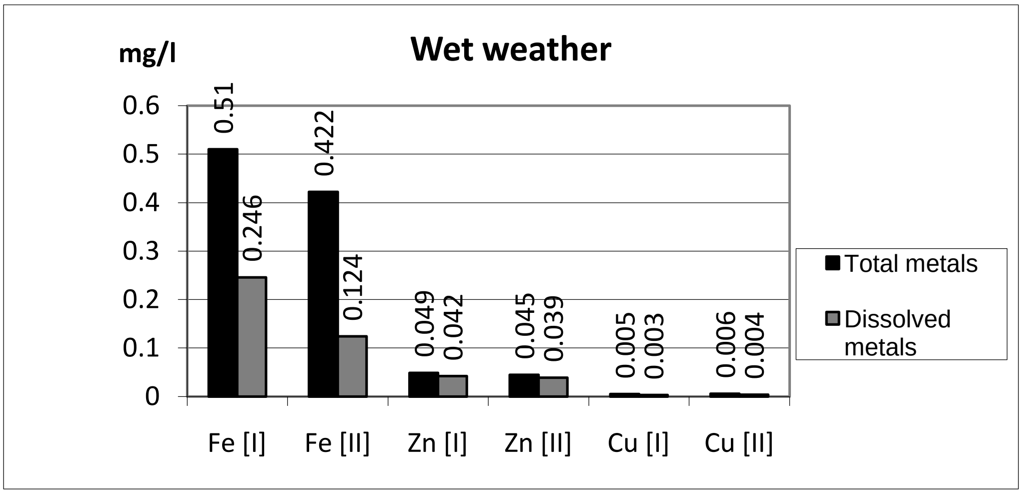


Fig. 6.29 The mean value of metals during wet weather: I – before sewage outfall; II – after sewage outfall

diluting effect and there is no impact on the Brook, which now has elevated metals as a result of the wet weather.

Comparing Figs. 6.28 and 6.29 as well as Table 6.16, it can be concluded that in dry weather metal concentrations are increased by sewage work final effluents, but in wet weather they have no effect. The same opinion was given by Bubb and Lester (1995), who concluded that during dry weather flow for Letchworth STW was a source of metals (Table 6.15). However, the picture might be different depending on the receiving water flow rate and upstream water quality together with the rainfall characteristics (rainfall intensity and duration). Bakri and Rahman (2008), for example, found that the share of stormwater runoff and sewage works heavily depended on the runoff coefficient, which was itself linked to ADWP. Rainfall in our measurements increased the background concentrations of metals.

6.4 WOODBROOK

The data obtained from Woodbrook during dry weather is shown in Table 6.17 and in wet weather in Table 6.18 (see Appendices 5 and 6 for details). A comparison with the metal content of two other local brooks is shown in Table 6.19. The percentage of metals in their soluble form is displayed in Fig. 6.30.

There was a wide range of concentrations for most parameters but an increase in iron and TSS was observed during wet weather, as might be predicted from the previous results and from the M1 data.

Taking the mean values (from Tables 6.17 and 6.18) for all conditions and species, then Fe was always at the highest concentrations, as might be expected and as noted from the M1. There was dilution or reduction in the concentration of the other key indicators, such as Zn, P and $NO_{3,}$ by the rain. Further work linking these pollutants to flow could reveal a model to predict their behaviour. Similar concentrations of Fe values during wet weather were reported by Mosley and Peake (2001) (Table 2.2), which were 3.419 mg/l and 0.211 mg/l for Fe_{tot} and Fe_{dis}, respectively.

Table 6.17 Data from Woodbrook during dry weather conditions (21 samples)

Contaminant, mg/L except pH, turbidity and EC	Range	$\overline{X}$	S	C_v
Iron (total)	Traces – 0.528	0.192	0.139	0.722
Iron (dissolved)	Traces – 0.222	0.046	0.058	1.26
Copper (total)	Traces – 0.022	0.008	0.008	1.0
Copper (dissolved)	Traces – 0.012	0.002	0.003	1.63
Zinc (total)	Traces – 0.109	0.035	0.031	0.868
Zinc (dissolved)	Traces – 0.019	0.005	0.007	1.42
Na	9 – 117.74	21.629	22.206	1.03
pH	7 – 8.17	7.69	0.396	0.052
TSS	2.45 – 29.0	7.7	6.524	0.845
Turbidity, NTU	0.198 – 15.5	3.31	3.585	1.08
TDS	200 – 510	280	66.153	0.239
EC, µS/cm	420 – 1010	545	124.68	0.229
TOC	3.45 – 19.08	8.15	3.975	0.488
Hardness	165 – 465	300	77.289	0.258
PO_4^{3-} **, as** P	Traces – 1.339	0.316	0.434	1.37
NO_3^-	15.792 – 28.081	21.859	4.069	0.186

Table 6.18 Data from Woodbrook during stormflow (rainfall events) conditions (12 samples)

Contaminant, mg/L except pH, turbidity and EC	Range	$\overline{X}$	S	C_v
Iron (total)	0.122 – 10.96	2.65	3.36	1.27
Iron (dissolved)	0.028 – 0.832	0.167	0.245	1.47
Copper (total)	Traces – 0.103	0.027	0.029	1.1
Copper (dissolved)	Traces – 0.006	0.002	0.002	1.0
Zinc (total)	0.012 – 0.202	0.079	0.049	0.62
Zinc (dissolved)	0.002 – 0.066	0.025	0.025	1.0
Na	9.35 – 52.92	21.21	12.387	0.584
pH	6.9 – 7.57	7.29	0.292	0.041
TSS	8 – 295	84.45	108.25	1.28
Turbidity, NTU	2.55 – 215	48.1	63.82	1.328
TDS	130 – 280	199	54.66	0.275
EC, µS/cm	260 – 550	397	102.96	0.259
TOC	5.85 – 69.4	22.45	19.385	0.852
Hardness	235 – 300	275	32.85	0.119
PO_4^{3-} **, as** P	Traces – 2.467	0.559	0.734	1.322
NO_3^-	8.28 – 22.881	16.09	5.358	0.333

During dry weather the Fe concentrations reported by Mosley and Peake were higher (Fe_{tot} = 0.674 mg/l and Fe_{dis} = 0.243 mg/l) compared to our data in Table 6.17 (0.19 and 0.046 mg/l, respectively), even though the TSS concentrations were almost the same, namely 6 mg/l for Mosley and Peake and 7.7 mg/l for our data. It is not surprising that iron is in the highest concentration, considering that Fe is the most abundant element in soil in a number of different types of minerals

(O'Neill, 1998) and is a common material for land drains. Mosley and Peake admitted that an additional source of iron in their case might have been the corrosion of metallic iron drainage pipes, though the studied catchment was deliberately chosen as one consisting predominantly of residential housing land with little industrial activity. The proportion of Fe in the dissolved form is relatively small compared to the total metal concentration, indicating that most of the Fe is affiliated with particulate matter (Fig. 6.30). The dissolved metal fraction $\boldsymbol{f_{dis}}$ obtained from the Fe values during wet weather (Fig. 6.30 and Table 6.18) is 6.3%, which is the same as Mosley and Peake's result, which was 6.4%. During dry weather the $\boldsymbol{f_{dis}}$ was 36% for Mosley and Peake and 23.9% for our data

Table 6.19 Average concentrations of the indicator metals in three local brooks in the M1 catchment

Metal, mg/l		Grace Dieu Brook (12 samples)	Black Brook (10 samples)	Woodbrook (21 samples)	**EQS, mg/l**
Iron	total	**0.28**	**0.281**	0.192	
	dissolved	**0.119**	0.048	0.046	**1.0**
Copper	total	0.006	0.004	**0.008**	
	dissolved	**0.003**	**0.003**	0.002	**0.01**
Zinc	total	0.026	0.014	**0.035**	**0.075**
	dissolved	**0.018**	0.008	0.005	

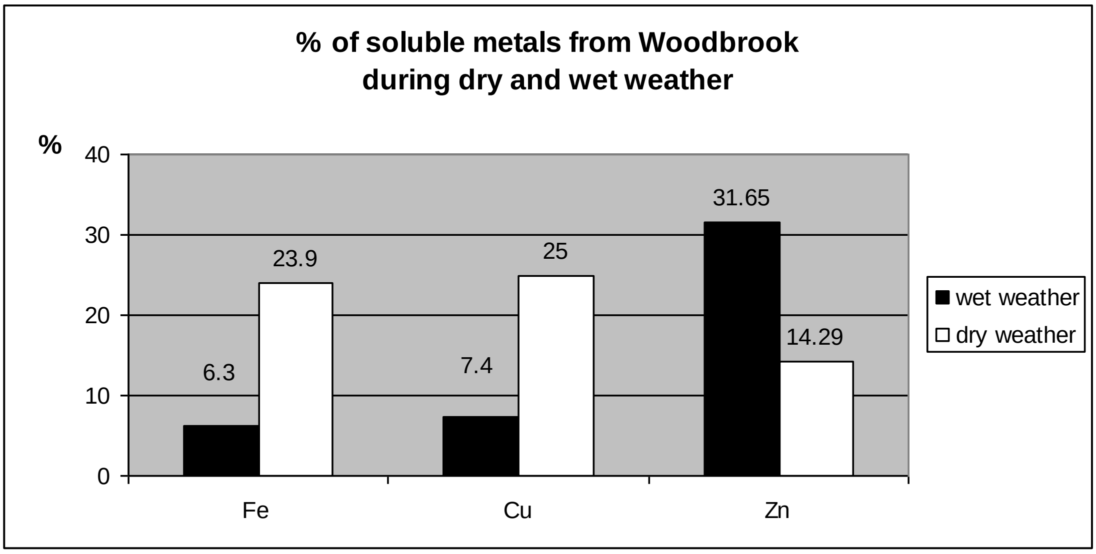


Fig. 6.30 Percentage of soluble metals

(Table 6.17). Wet weather flushed out solids and associated total iron, thereby reducing the proportion of dissolved iron fixed by its solubility. The iron concentrations in Woodbrook were similar to those in the runoff from the M1, i.e. 2.65 mg/l and 2.104 mg/l respectively, although the range in Woodbrook is greater.

Zn was the next most common metal, which confirmed the results of analyses reviewed in the literature survey (see section 2.4, Table 2.2), and it was found with a high proportion in the dissolved form. The f_{dis} for Zn during wet weather determined by Mosley and Peake was 0.47 (47%), which was higher again by comparison with our data (32 %) (see Fig. 6.30). The f_{dis} value obtained from the study of Berretta et al. (2008) was 13% (see section 2.4, Table 2.2). The explanation as to why Beretta et al (2008) found such a low proportion of Zn in the soluble form can be attributed to the high TSS value of 226.9 mg/l that they determined, which was 2.5 times higher than either that from our data or from Mosley and Peake. This data implies that even though Zn has been found predominantly in its dissolved form, it is also bound to solids, depending on the TSS concentration. In dry weather the pattern is different, with 14% of the zinc dissolved, which is lower than the corresponding proportions for the other metals. This suggests that Zn shows more complex behaviour with solids and water chemistry (pH solids) which might be associated with the amphoteric property of zinc at different pH. This needs more research. These proportions are only slightly different for motorway runoff, in which the Zn was 21.1% soluble for dry weather and 26.24% for wet weather, implying that the ligands might be the same.

The behaviour of Cu in this study does not agree with other research on urban and residential runoff because the concentrations found are much lower. The most likely explanation is that, in our case, Woodbrook is predominantly a rural stream in which the conditions are pristine. Most of the literature reviewed was focused on urban environments with higher copper concentrations. The f_{dis} value for Woodbrook was 0.074 (Table 6.18) during wet weather, whereas Mosley and Peake (2001) and Beretta et al. (2008) reported the f_{dis} as 0.43 and 0.35, respectively. Our data shows that Cu behaviour is similar to that of Fe, suggesting solid binding (see Fig. 6.30). Another possible explanation for such a difference in the f_{dis} value for Cu could be the application in our case of the microwave digestion technique for total metal recovery. To try to decide whether the chosen control brook was unusual two other brooks, though still rural, in the same overall catchment and a few kilometres from the M1 were also sampled.

Table 6.19 compares these three local brooks in the same catchment (Woodbrook, Grace Dieu Brook [upstream of the sewage works] and Blackbrook) during dry weather. The total metal concentrations reported in this table are a comparison from hot plates for Grace Dieu Brook and Black Brook and from microwave digestion for Woodbrook. Assuming that microwave digestion recovers more total metals, then these values should be greater, particularly for copper (see section 6.1). One can see that the use of microwave digestion may have increased the recovery of Zn and Cu but not Fe. Thus, this provides some evidence to explain the unexpected and variable copper results for Grace Dieu Brook and Blackbrook and those of other researchers. Hot plate analysis may therefore be more vulnerable to atmospheric contamination than volatilisation or other reactions occurring in the hot plate. This needs more work but it reinforces the suggestion stated in section 6.1 as to how important the choice of analytical technique is.

Another feature of all the data is that the background concentrations of the metals are as expected within the EQS. Throughout the whole period of the study, including wet weather, the EQS concentration of the total Zn was exceeded once during wet weather (15/04/2009) (Zn_{tot} = 0.202 mg/l, EQS for Zn_{tot} is 0.075 for hardness values from 200 to 250 mg/l). Dissolved Cu was also exceeded once during the storms on 15/01/2008 (Cu_{dis} = 0.022 mg/l, EQS for Cu_{dis} is 0.01 for hardness values from 200 to 250 mg/l). Table 6.19 shows the average data.
In comparison to the samples from the M1, those from the lagoon never exceeded the EQS for the 3 indicator metals (sampling point 4; Fig. 4.2 b).

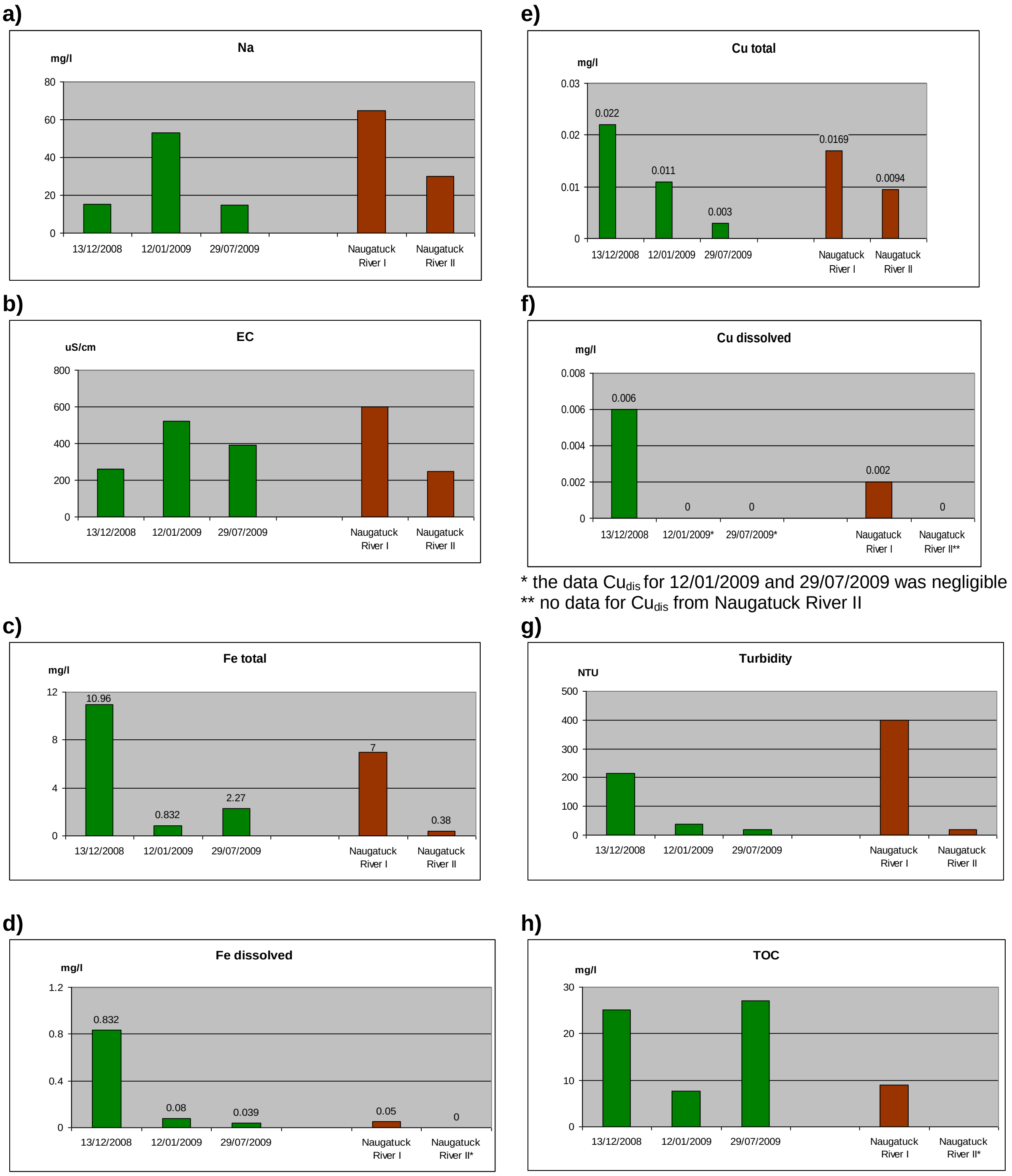
Another feature of the data is that the values of the coefficient of correlation (C_v) for the TSS, and turbidity and total metals (0.62 for Zn_{tot} to 1.33 for turbidity) (Table 6.18) are greater than those obtained from the M1 discharges. This can be explained by the fact that random grab samples were used during wet weather and collected at different times during the rainfall events. The concentrations of metals would be expected to vary during the storm event, as noted from the M1 data, and ‘the first flush’ may not have been captured. The hydraulic conditions in natural brooks will be heterogeneous and during wet weather (depending on the flow rate and velocity) different particles will be re-suspended from the bottom of the brook, which results in a TSS increase. Determining the correlations between metals and flow rates as well as TSS and turbidity is the next stage in a model using dedicated flow measurement at the sampling site.

Fig. 6.31 shows, as an example, 3 grab samples taken during 3 different rainfall events, 2 of which are in winter. This was compared with other data reported by Morrison and Benoit (2005), for two reasons: their study analysed the same metals (Fe and Cu) and they also reported information about PSD. The study describes two sampling sites at the Naugatuck river: one was situated below the City of Torrington (Connecticut) (Naugatuck River I), so that it included the runoff from the city itself with its industry and sewage works, and the second site was chosen above the city (Naugatuck River II). Data was also presented from a rain-on-snow event in March. The first sample point (Naugatuck River I), as noted, receives all the urban drainage from 147 km^2, while the second one (Naugatuck River II) serves an area of 24 km^2 upstream of the City, which is comparable with Woodbrook (25.5 km^2). The background concentrations of pollutants upstream and downstream of the City (for the Naugatuck River) are presented with the corresponding data from Woodbrook in Table 6.20.

The data obtained for Na and EC from the 12/01/2009 Woodbrook sample were higher compared to the two other storm events as well as the mean values from Table 6.18, which was caused, we suggest, by de-icer salt in runoff even though the catchment is rural. A similar but stronger effect can be seen from the results obtained by Morrison and Benoit (2005) from the Naugatuck River where the presence of de-icer salt was the cause of increases in Na and EC (Fig. 6.31 a and b and Table 6.20). In Connecticut state the weather conditions are more severe and the concentrations greater.

The measured parameters in Woodbrook and Naugatuck River upstream of the urban area are of a similar range (Fig. 6.31 and Table 6.20). In this data turbidity showed a good correlation with total metals (Fig. 6.31 g) and the storm on 13/12/2008 showed the maximum value.

In our data Fe showed a good correlation with TSS Fe and turbidity among all the observed rainfall events throughout the studied period (Table 6.18).



* the data Cu_{dis} for 12/01/2009 and 29/07/2009 was negligible
** no data for Cu_{dis} from Naugatuck River II

* no data from Naugatuck River II

* no data from Naugatuck River II

Fig. 6.31 Comparison of water parameters and pollutants from Woodbrook on the left and Naugatuck River during selected storm events

It can be concluded that the concentration of total metals depends on TSS and turbidity, as can be seen in both the Woodbrook and Naugatuck River data. The impact of the urban environment on the Naugatuck River is demonstrated in every parameter. Fig. 6.31 g shows turbidity (Naugatuck River II to Naugatuck River I) ranging from 20 to 400 NTU respectively. The authors concluded that this was due to the urban runoff.

Table 6.20 Background concentrations of selected water quality parameters from urban runoff in Connecticut* and Woodbrook during dry weather

Sampling points	EC, µS/cm	Na_{dis}, mg/l	Fe_{tot}, mg/l	Cu_{tot}, mg/l	TOC, mg/l
Naugatuck River I	300	20	0.1	0.002	6
Naugatuck River II	40	10	0.19	0.002	No data
Woodbrook	545	21.6	0.192	0.008	8.15

* modified from Morrison and Benoit, 2005

TOC concentrations in the Naugatuck River (downstream) are comparable with those from the unpolluted control stream (Woodbrook) used in this study. The value of 9 mg/l (Fig. 6.31 h) from the Naugatuck River was similar to the overall average recorded in Woodbrook and it supports the similarities in catchment.

Table 6.21 summarises the results of particle size distributions found in samples taken from Woodbrook during dry (13/02/2007) and wet weather (15/01/2008). From this table it can be seen that there is an increase in particles of sand (known as sand by BSI), for example, > 80 µm, (18.62 %) particles in the brook during the rainfall event compared to 6.73 in dry weather. The proportion of fine particles (defined as clay by BSI) during wet weather is reduced to 2.07 % (1.88 +0.19), compared to 4.97 % (3.86 +1.11) in dry weather, presumably due to dilution and flushing.

Table 6.21 Particle classes and size ranges of Woodbrook samples

Particle class **BSCS 5930:1981**	Particle class size range	Particle size distribution,%	
		13/02/2007 dry weather	15/01/2008 rain
Sand	> 80 µm	6.73	18.62
Coarse silt	20 – 80 µm	42.01	30.97
Fine silt clay	1 – 20 µm	46.29	48.34
Clay and large colloids	0.45 – 1.0 µm	3.86	1.88
	0.45µm and less	1.11	0.19

Fig. 6.32 compares the results for metal solubility from the wet (15/01/2008) and dry weather (13/02/2007).

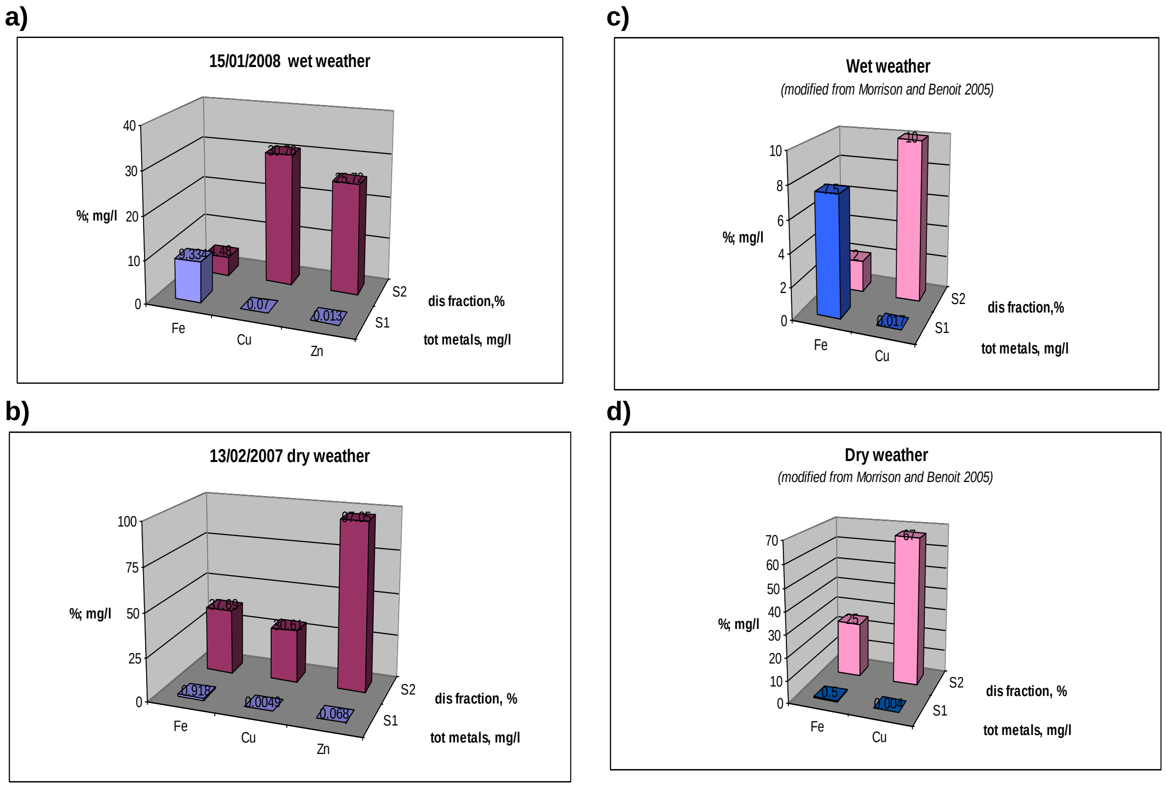


Fig. 6.32 Particle size associations for metals from Woodbrook and the Morrison and Benoit study

Morrison and Benoit (2005) also present data on the detailed analysis of Cu and Fe associations with particles throughout a rain-on-snow event from 13th March to 15th March 2001 and these are shown in Fig. 6.32 c and d**,** Table 6.22. The four samples, chosen for detailed size distribution analysis, represent different times within the event (see the footnote to Table 6.22), i. e: I – pre-event baseflow; II – peak flow (first part of the storm); III – second shower event; IV – post-event flow. Both our Woodbrook data, shown in Fig. 6.32 a (wet weather), and the Naugatuck River data show that 10 – 30 % of Cu is dissolved compared to Fe, which ranges between 2 and 4.5 %.

From Table 6.22 in the Naugatuck River one can see that in most cases Cu was bound with fractions which were less than 0.45 µm (from 58% to 67%) except at the peak flow (column II), where the dissolved fraction was only 10%. The comparable dissolved fraction for Cu obtained from the wet-weather Woodbrook was 30.61% (Fig. 6.32 a), which was half that reported by Morrison and Benoit (2005; Table 6.22).

Fig.6.32 a and b show that there is almost no change in the dissolved Cu in Woodbrook between dry and wet weather compared to iron and zinc. Both data sets are from winter, but the sample taken on 13/02/2007 was taken after the melting of snow which had fallen on 09/02/2007. This suggests that de-icing salt was present (EC = 460 µS/cm, compared to 300 µS/cm) on 15/01/2008 which, according to the previous data, would have increased the dissolved phase metal concentrations. Dissolved Fe increased from 4.48 to 37.69% and Zn from 25.72% to 97.05%. Bubb and Lester (1995), studying the behaviour of metals in sewage effluent and river surface water in Bedfordshire, UK, found no correlation between soluble copper and chloride. Their data, however, were from steady states with no sudden changes in either dissolved salts or flow.

Our data, supported by Morrison and Benoit (2005), imply that TSS concentration can play a significant role in metal behaviour, particularly that of Fe, but even in the cases of metals which other researchers have found predominantly in the dissolved form. Future research on the potential chelating chemical present in different types of surface water should provide information for an improved model. The Morrison and Benoit data, however, are unusual because they are from a cold region. The use of de-icer has been shown to affect the results.

Table 6.22 Percentage changes in particle size distribution associated with selected metals

Particle class and size range	Copper (Naugatuck River I)				Iron (Naugatuck River I)				Iron (Naugatuck River II)			
	I	**II**	**III**	**IV**	**I**	**II**	**III**	**IV**	**I**	**II**	**III**	**IV**
Sand > 80 µm	11	-	7	18	20	5	5	-	15	35	35	30
Coarse silt 20 – 80 µm	19	72	12	17	30	86	60	49	18	15	30	34
Fine silt clay 1 – 20 µm	-	14	12	3	-	3	1-0	10	5	5	-	10
Clay and large colloids 0.45 – 1.0 µm	3	3	4	4	20	4	10	15	20	15	17	8
0.45 µm and less	67	10	65	58	30	2	10	26	42	30	18	18

I – pre-event baseflow; **II** – peak flow (1st part of the storm); **III** – second shower event; **IV** – post-event flow.

The graph (Fig. 6.32 a) shows that during storm runoff the dissolved form of Fe was less than 5% of the total metal, as a consequence of the presence of increased solids, whereas during dry weather the soluble part of Fe was 37.69 %,

(Fig. 6.32 b). Similar results for iron were obtained by Morrison and Benoit (2005) (Fig. 6.32 c and d and Table 6.22).

We hypothesise on the basis of our data that Zn behaviour (its binding to particulate matter) is strongly dictated by the presence of the de-icer salts. Fig. 6.32 b shows that almost the whole Zn concentration in Woodbrook in cold weather was attributable to dissolved Zn (97.05 %)*. Zn values were not reported by Morrison and Benoit (2005).

Gundersen et al. (2001), studying the seasonal variations in Zn in mine-polluted streams, observed several rain- and snow-melt-induced peaks which progressively reduced the dissolved fraction of Zn. This may be explained by the fact that ions (Na^+) were not present.

Thus, the summary of the results from this section is presented in Table 6.23 in comparison with other sampled test sites (M1 and LSW), as well as the EQS.

Table 6.23 Averaged results from the M1, Woodbrook and LSW

Metals, mg/l	Wet weather		Dry weather		LSW	EQS
	M1	Woodbrook	M1	Woodbrook		
Iron (total)	2.104	2.65	1.119	0.192	0.06	
Iron (dissolved)	0.124	0.167	0.103	0.046	0.033	1.0
Copper (total)	0.045	0.027	0.005	0.008	0.005	
Copper (dissolved)	0.008	0.002	0.002	0.002	0.004	0.01
Zinc (total)	0.141	0.079	0.057	0.035	0.06	0.075
Zinc (dissolved)	0.037	0.025	0.012	0.005	0.051	

During dry weather, the concentration of Fe_{tot} and Fe_{dis} was higher compared to Loughborough sewage works but less than that found in the lagoon. The Cu_{tot} concentrations from Woodbrook had the highest value observed (0.008 mg/l), compared to both the lagoon and Loughborough sewage works. The explanation may be that the sampling point in Woodbrook was in the vicinity of the road where

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* It should be noticed that total metal recovery was done by hot plate, which might have resulted in incomplete Zn digestion, and the reported "total concentration" (see Table 4.5) is likely to be less than the actual value.

vehicles had to brake because of a traffic light. Dissolved copper had the same value as in the lagoon but dissolved copper in LSW was twice as abundant as in the brook and the lagoon. Zinc concentrations in Woodbrook had their lowest values, compared with the lagoon.

During wet weather the concentrations in Woodbrook increased and the Fe concentrations were even slightly higher than those from the M1. The total zinc concentration was 0.079 mg/l, which was lower than that from the M1 (0.141 mg/l), but it exceeded the EQS for Zn_{tot} (0.075 mg/l). The total copper concentration increased 3.5 times but it was 2 times lower than from the M1. Dissolved copper remained the same as during dry weather (0.002 mg/l).

The results also show that sub-zero temperatures affect metal solubility if de-icer is applied, which has been supported by data from Connecticut State (Morrison and Benoit, 2005).

Rainfall events generate an increase in coarse particles (> 80μm) compared to dry weather because of the flushing or re-suspending of particles from the bottom of the stream. However, the percentage of smaller particles decreased during wet weather, possibly because of the dilution effect.

The results obtained in this section show that wet weather has an effect on metal solubility (see Fig. 6.30) which might be linked with the percentage of PSD. However, the results also showed that weather and local conditions can confound this simple interpretation. Fe and Zn solubility increased for the winter conditions analysed (Fig. 6.32 a and b) and Cu in its dissolved phase increased for samples taken during wet weather. Metal solubility increased both as a result of evaporation (Fe) and also due to re-solubilisation from the sediment (Zn and Cu).

Thus, to summarise the results from this section, it has been concluded that wet weather has a greater effect on background or natural water quality than treated urban inputs. The extent of the change in metal concentrations (and other water quality parameters) was shown to depend on rainfall characteristics but also on sub-zero temperatures. Our studies, in common with those from Connecticut, suggest that NaCl from de-icer increases the Cu concentration in urban runoff.

Iron was shown, as in previous work, to be in the highest concentrations in both pristine streams and urban runoff, typically ten times the concentration of the next most common metal, zinc. In dry weather the sewage work discharges of metals into the catchment were greater than those measured from the treated M1 runoff. The sewage work effluent concentrations were below the EQS (0.1 mg/l for Fe_{dis}, for example, compared to the EQS for Fe_{dis} 1.0 mg/l). In wet weather our results suggest that stream water quality is improved by the sewage work effluent. The results from the M1 have suggested that ADWP is the most important influence on metal concentration in runoff. The combination of interceptor and lagoon used at the M1 site to achieve these standards may be too large for some highway locations. Therefore, as reported in the next section of the thesis, an alternative combination of separator and filtration as suggested in PPS 25 was investigated.

6.5 FILTRATION

Throughout several groups of filtration experiments the following results were typical and can be summarised for the two media - glass and gravel - as follows:

1. The lowest velocity in the experiment was 2 m/hr (the velocity of filtration in this study varied from 2 to 8 m/hr) and such low velocities were ineffective for dissolved metal removal.
2. The first sample point (1st tap) for all periods of time and parameters (except dissolved metals) gave the poorest quality results, as might be expected, whereas the final effluent (at the bottom of the filter) almost always showed the highest percentage of metal removal.
3. The results demonstrated that metal removal was linked to the removal of TSS which were retained in the filter and formed sediment.
4. TSS also accumulated at the filter surface on the top layers. The concentration of TSS as well as total metals increased in the top of the filter first and progressed down the filter, following classical filtration theory (Ives, 1990).

5. The last sample from an experimental run always had the poorest quality due to sediment enrichment from the tank bottom. The water quality decreased with run time, as expected.

The sediment mass added into the system was based on an added TSS concentration of 100 mg/l. This concentration has never been observed during a wet weather sampling period at our chosen sampling points at the outlet of the interceptor and it was selected based on the literature for the sake of achieving greater reproducibility of the experiment. However, the actual measured initial concentration varied both throughout a filter run and from filter run to filter run so that, despite the use of a standard preparation, it was measured to be from 40 to 400 mg/l. The difference between actual and estimated concentrations can be explained by the adhesion of the sediment to the walls of the tank as well as its being deposited by settlement within the system (upper tank, pipes) (see Chapter 5, Fig. 5.1 and Photo 5.1).

As an example, Figs. 6.33 – 6.39 present the results from the first filter run (crushed glass medium) (30/07/2008). The medium was analysed for the background level of pollutants and washed thoroughly prior to these, the first experiments (see section 5.1).

From Fig. 6.33 it can be seen that the 1^{st} sample point (the 1^{st} tap), the upper 20 cm of the glass, had the highest concentration of TSS, as was to be expected, since this received the largest amount of TSS.

Solid accumulation during the first hour at the 1st sampling point was twice as great as at the other sampling points (2^{nd} tap – FE) and around 7 times higher during the second and third hours of filtration. This coincides well with the patterns both of turbidity and the Fe_{tot} results (Figs. 6.34 – 6.35).

Figure 6.35 demonstrates that Fe_{tot} had the strongest links to TSS and consequently it was retained on the sediment. Total zinc and copper showed less

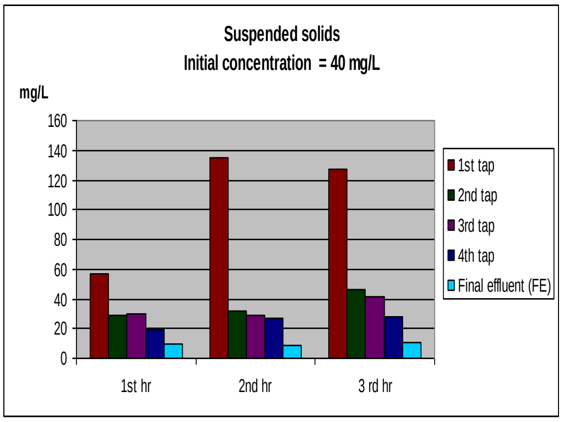


Fig. 6.33 Concentration of TSS taken from the sample points of the column

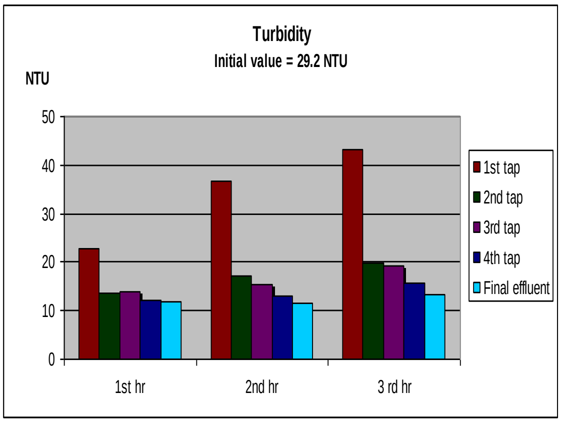


Fig. 6.34 The values of turbidity taken from the sample points of the column

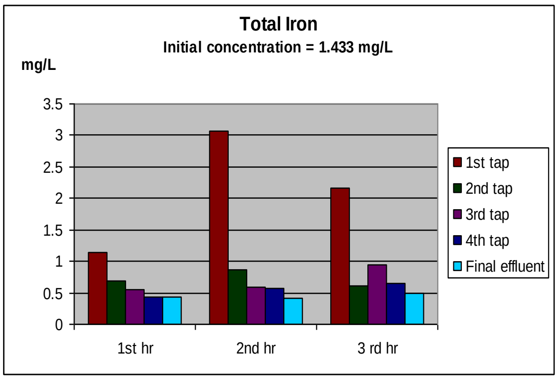


Fig. 6.35 Concentration of total iron taken from the sample points of the column

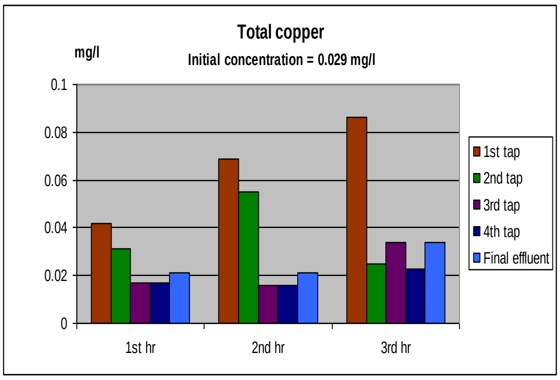


Fig. 6.36 Concentration of total copper taken from the sample points of the column

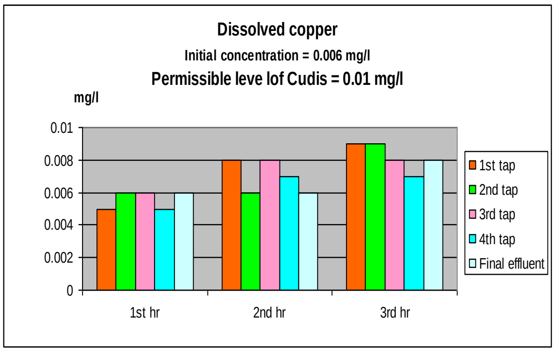


Fig. 6.37 Concentration of dissolved copper taken from the sample points of the column

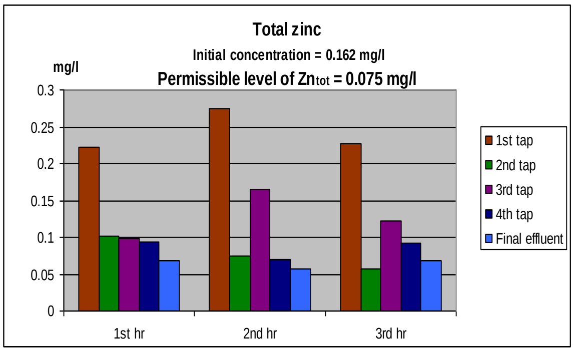


Fig. 6.38 Concentration of total zinc taken from the sample points of the column

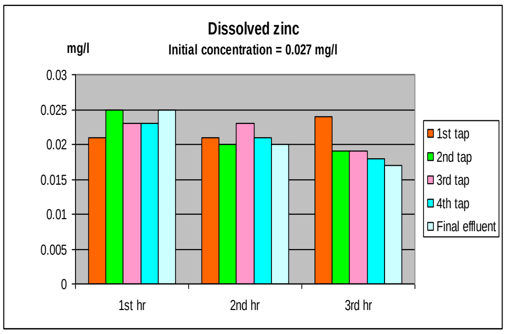


Fig. 6.39 Concentration of dissolved zinc taken from the sample points of the column

affiliation with particles, as was shown previously in runoff and the control brook, while TSS decreased gradually (Fig. 6.33).

These figures would also be representative of any solid-associated pollutant accumulation in the media surface or the top layers (to a 20 cm depth from the top of the media). This is normal in filtration and it is known as “cake formation”, the assumption being that it is due to the concentration gradient.

Figures 6.37 and 6.39 show that dissolved copper and zinc concentrations remained the same throughout the filtration run, compared to the initial concentrations, which were 0.006 and 0.027 mg/l respectively. These results were expected on the basis of previous experiments (see section 6.2), where it was shown that dissolved metals did not change significantly with changes in TSS during a rainfall event (equivalent retention time for a storm and in the filter run). A much longer retention time in the filter may be needed for dissolved metals or more complex chemical interactions to occur between contaminants and filter media, for example, as shown with salts (see section 6.2).

Clark et al. (2005) compared both downflow and upflow columns and found that downflow columns were less effective than upflow columns. Moreover, having conducted the experiment with upflow filtration, it was concluded that more stormwater might have been treated and filtration runtime could have been extended before clogging. It was confirmed that the sediment that accumulated in the bottom of the media fell away into the sump after the flows had stopped. The paper does not provide any information about the velocity of filtration or the PSD of stormwater.

Figs. 6.40 and 6.41 compare the effectiveness of total Zn removal using crushed glass and gravel. In both figures the bold line represents the ratio of the permitted concentration to the average feed concentration C_{infl}, as an indicator of filtration performance. The permissible concentration of EQS of total Zn is 0.075 mg/l for hardness levels ranging from 100 to 250 mg/l $CaCO_3$.

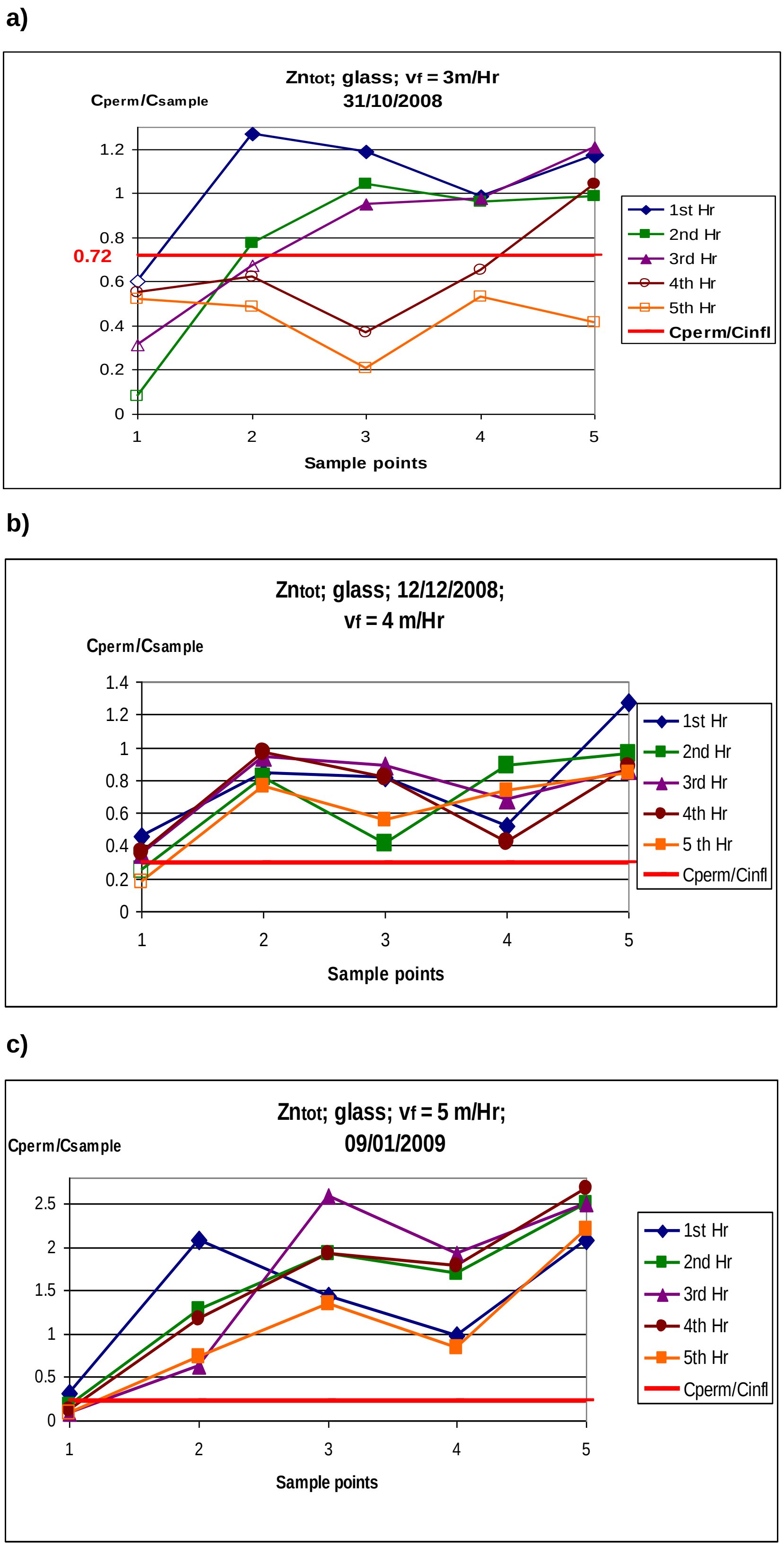


Fig. 6.40 Filtration performance for total Zn removal by crushed glass

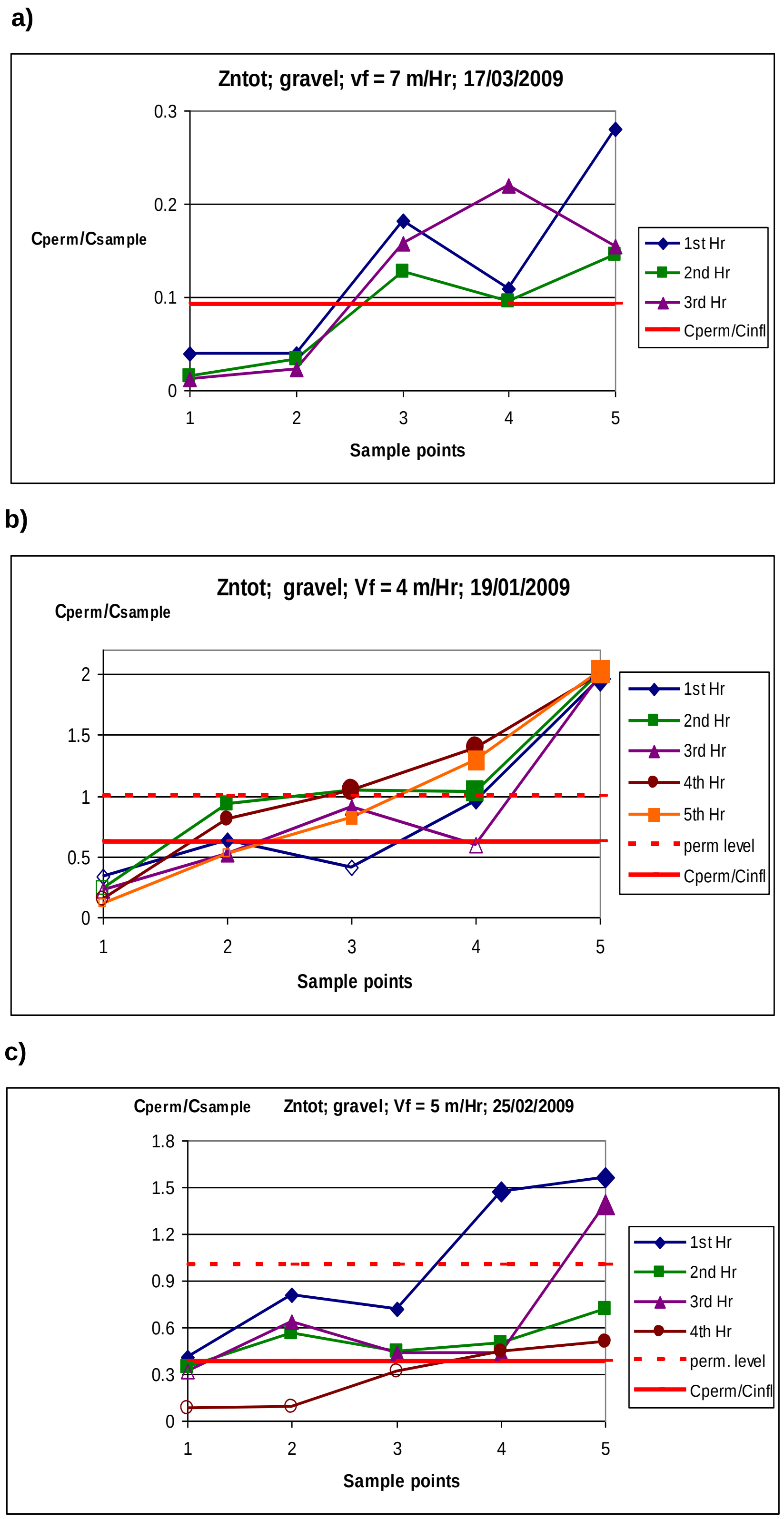


Fig. 6.41 Filtration performance for total Zn removal by pea-gravel

The C_{infl} values were calculated as the sum of the feeding concentrations divided by the number of hours run.

From these figures one can see that the values of the line indicating filtration performance criteria will depend on the initial feeding concentration. The greater the feeding concentration, the better the filtration performance would be expected to be. Thus, the larger the ratio, the better the performance will be. Fig. 6.40 a, for example, where $\frac{C_{\mathrm{perm}}}{C_{\mathrm{infl}}} = 0.72$ (average feed concentration = 0.104 mg/l), demonstrates that after 3 hours of filtration the quality obtained from glass filtration deteriorated at each sampling point (4th and 5th hours). Fig. 6.40 a, b and c represent the effectiveness of crushed glass during 5 hours of filtration with filtration velocities of 3, 4 and 5 m/hr, respectively, and an inverse relationship between velocity and performance is demonstrated.

Fig. 6.41 a, b and c, represent the efficiency of pea-gravel during 3, 5 and 4 hours filtration with filtration velocities of 7, 4 and 5 m/hr, respectively. Values above the line show a good filtration performance, but this does not necessarily achieve the EQS. Values below the line indicate a poor filtration performance and deterioration in the water quality.

This progressive accumulation was less strong in the pea-gravel media, probably due to their higher porosity and consequently better retention of sediment and deeper penetration into the medium itself. However, Fig. 6.41 a shows that the worst performance of a pea-gravel medium occurred at the highest rate, when the concentration at the 5th sample point (FE) did not achieve the EQS, which supports the idea of the medium clogging with time. This filter run was conducted on 17/03/2009, whereas the two earlier runs (Fig. 6.41 b, c) were carried out on 19/01/2009 and 25/02/2009, respectively, and showed a better performance

It can be seen that the total Zn concentration varies widely both in crushed glass and pea-gravel media (Figures 6.40 and 6.41) and from sample point to sample point. Generally, the first sample point during the run was almost always below the line, representing an unsatisfactory filtration performance. The final effluent (FE – 5th sample point) was almost always both above the line and able to achieve the EQS. The fifth sample point for all pollutants for both glass and pea-gravel media always had the highest performance. Zn_{tot} concentrations at all other sampling points were irregular, which can be explained by the fact that the sediment moved up and down the column according to small perturbations in the flow.

It was expected that the total zinc concentration would increase with time, i.e. the performance would deteriorate with hours of run. One can see that at the 3rd sample point during the 3rd hour (Fig. 6.40 **c**) total Zn had the lowest concentration observed. Sediment accumulated and was left between runs, since backwashing columns were not included. Backwashing was avoided deliberately, since it would be unlikely for media backwashing of filters to act in the field.

Fig. 6.42 a, b, c and d show the performance of filtration using crushed glass for the other pollutants (TSS, Fe_{tot} and Cu_{tot}) and they correspond with Fig. 6.40 c, whereas Fig. 6.43 a, b, c, d and e match the conditions shown in Fig. 6.41 b but using pea-gravel. The permissible level for TSS was chosen as 10 mg/l, which was selected as a potential initial concentration for the second step filtration after an interceptor. The permissible level for Fe_{tot} was chosen as the background Fe_{tot} concentration in the lagoon, since there is no formal standard for iron. The corresponding TSS concentration ranged from 7 to 14.5 mg/l (21 samples) and constituted 0.5 mg/l of Fe_{tot}.

The permissible level for Cu_{tot} was calculated from the values corresponding to the EQS for Cu_{dis} (0.01 mg/l) and the corresponding values in the lagoon were 0.048 mg/l (10 samples).

Comparing these Figures one can see that the best correspondence with TSS was with Fe_{tot} in both glass and gravel, as might be expected, whereas the worst affiliation with TSS was with Cu_{tot} as would be anticipated from the previous results on the solubility of Fe, Zn and Cu. Clark et al. (2005) studied metal removal using mixtures of peat-sand, compost and zeolite media. It might have been expected that the organic mixes that Clark et al. (2005) used would show a better performance than simple glass, sand or gravel. Other work on colour removal

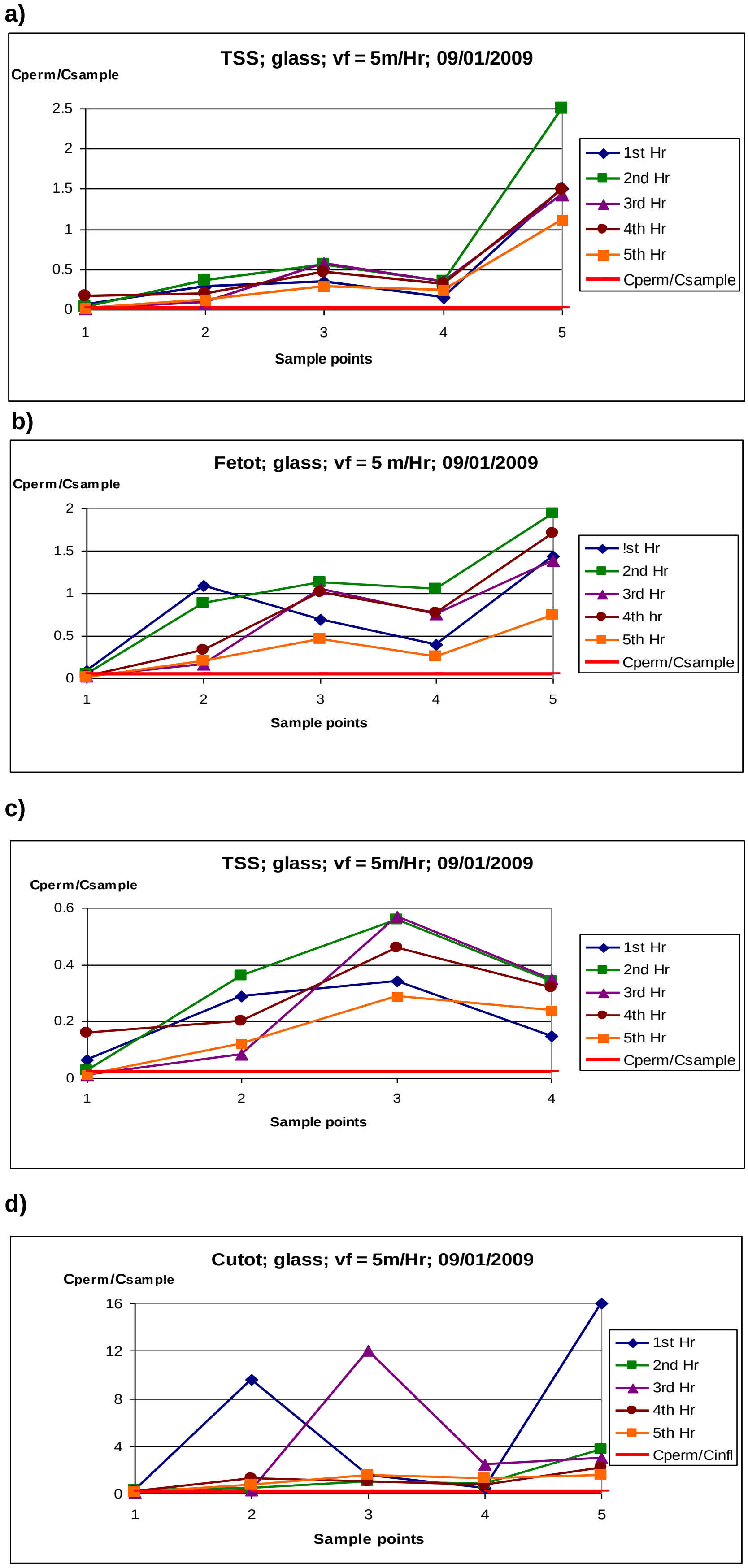


Fig. 6.42 Filtration performance for removal of some pollutants by glass

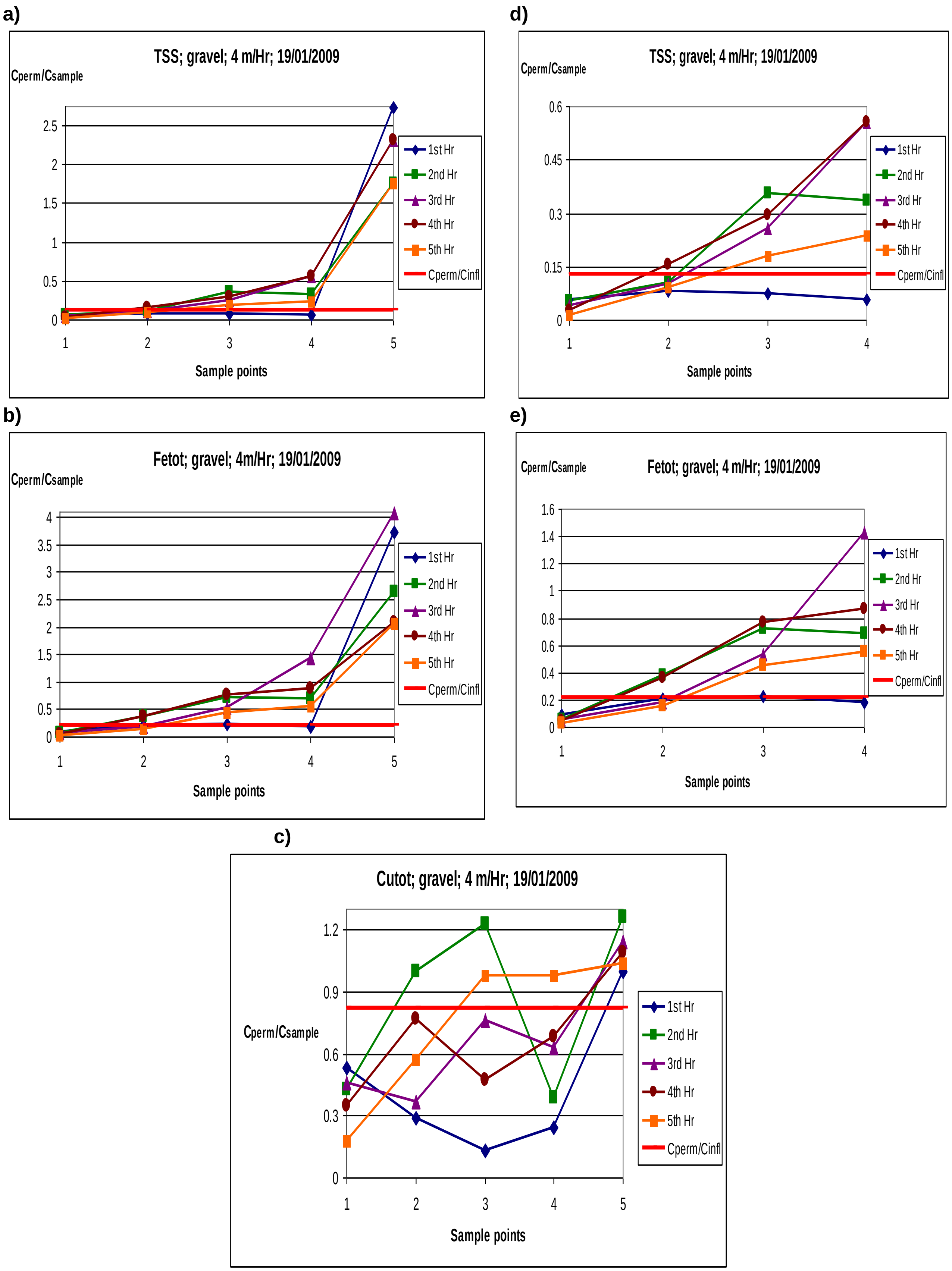


Fig. 6.43 Filtration performance for removal of some pollutants by pea-gravel

(Cairns et al., 2009) has indicated that a charged surface, as might be expected, can remove dissolved materials, NOM in particular.

Tables 6.24 (2nd filter run) and 6.25 (7th filter run) represent the data for crushed glass and pea-gravel for 3 hours of filtration with a filtration velocity of 7 m/hr.
Tables 6.26 and 6.27 present a similar comparison of glass and gravel but from a later run at a lower filtration rate of 4 m/hr. The initial concentration of pollutants was, unfortunately, different each time because of the difficulty in managing the feed material. The bold blue values represent the achievement of the EQS. The bold black values represent the deterioration in the media quality.

Comparing the effectiveness of crushed glass at different velocities (7 and 4 m/hr) (Table 6.24 and 6.26), it can be suggested that the data shows a progressive accumulation of the solids in the filter bed until breakthrough. Although the final TSS in the second run (Table 6.26) at a lower velocity is better, in the final effluent the retention of metals is not as good and neither is the solid quality at other points. Both metals and solids show greater accumulation in the second run despite or because of the lower velocity. The breakthrough of solids would have been anticipated if the filter run had been continued. Taking into consideration the conditions of the experiment (the absence of backwash), it can be suggested that the overall effectiveness of TSS removal top to bottom improved at the lower flow rate (Table 6.26). The differences between the two runs were, however, compromised by the reduction in TSS (116.2 mg/l, run 1, to 48 mg/l, run 2), which could bias the result in favour of the second run.

Table 6.24 shows solid accumulation and wash out in the first 0.4 m of the filter after 3 hours using a TSS typical of stormwater runoff. The analysis of the data represented in Table 6.26 suggests that solids were also accumulating from run to run, as might be expected, with a more rapid deterioration in the intermediate samples despite the lower velocity. The overall effectiveness of the pollutant removal increased across the whole filter, but this would also eventually be expected to deteriorate as the filter became full of solids.

Table 6.24 Pollutant treatment efficiency of artificially prepared stormwater depending on the medium height (glass), %. (Velocity of filtration 7 m/hr; C_{TSS} = 116.2 mg/l; C_{Fe} = 4.1 mg/l; C_{Cu} = 0.091 mg/l; C_{Zn} = 0.222 mg/l)

Pollutant	Efficiency of the treatment under the duration of the filtration		
	1 hr	2 hr	3 hr
Final effluent (sample point 5)			
TSS	79.3	69.9	76.2
Fe_{tot}	73.1	62.9	73.5
Zn_{tot}	55.4	42.3	61.7
Cu_{tot}	**63.7**	16.5	**58.2**
Medium height 1.2 m (sample point 4)			
TSS	54.7	-98	40.2
Fe_{tot}	44.5	-87.5	40.2
Zn_{tot}	41.9	-49.5	32.9
Cu_{tot}	41.8	-39.5	27.5
Medium height 0.8 m (sample point 3)			
TSS	28.6	10.9	38.1
Fe_{tot}	49.7	19.8	46.1
Zn_{tot}	34.7	13.1	33.8
Cu_{tot}	**47.2**	14.3	27.5
Medium height 0.4 m (sample point 2)			
TSS	28.86	32.4	-47.6
Fe_{tot}	23.4	40.8	-76.9
Zn_{tot}	15.3	34.7	-41.5
Cu_{tot}	19.8	20.9	-43.9

Table 6.25 Pollutant treatment efficiency of artificially prepared stormwater depending on the medium height (gravel), %. (Velocity of filtration 7 m/hr; C_{TSS} = 80 mg/l; C_{Fe} = 2.95 mg/l; C_{Cu} = 0.065 mg/l; C_{Zn} = 0.82 mg/l)

Pollutant	Efficiency of the treatment under the duration of the filtration		
	1 hr	2 hr	3 hr
Final effluent (sample point 5)			
TSS	81.8	72.5	80
Fe_{tot}	**89.2**	76.4	**84.8**
Zn_{tot}	**67.1**	36.5	**40.9**
Cu_{tot}	**26.2**	-30.8	**44.6**
Medium height 1.2 m (sample point 4)			
TSS	-13.8	-60	53.8
Fe_{tot}	-29.3	-99.6	48.7
Zn_{tot}	16.1	5	47.8
Cu_{tot}	-6.2	-12.3	**41.5**
Medium height 0.8 m (sample point 3)			
TSS	-21.3	-1.3	-25
Fe_{tot}	-51.5	-1.8	-51.9
Zn_{tot}	**49.8**	28.6	**41.7**
Cu_{tot}	-4.6	9.2	0
Medium height 0.4 m (sample point 2)			
TSS	-276	-220	-370
Fe_{tot}	-276	-282	-554
Zn_{tot}	-127	-177	-307
Cu_{tot}	-149	-120	-191

The data for pea-gravel (Tables 6.25 and 6.27) was better because of the higher porosity of the media and the effectiveness of pollutant removal was better in the earlier filter runs (Table 6.25), even though the velocity was lower in the 2nd run

Table 6.26 Pollutant treatment efficiency of artificially prepared stormwater depending on the medium height (glass), %; velocity of filtration 4 m/hr; C_{TSS} = 48 mg/l; C_{Fe} = 1.23 mg/l; C_{Cu} = 0.032 mg/l; C_{Zn} = 0.098 mg/l

Pollutant	Efficiency of the treatment under the duration of the filtration			
	1 hr	2 hr	3 hr	4 hr
Final effluent (sample point 5)				
TSS	**88**	**87.5**	69.3	80.2
Fe_{tot}	**83.9**	**68.3**	**60.9**	56.4
Zn_{tot}	**34.6**	22.4	**36.7**	**26.5**
Cu_{tot}	**62.5**	**56.3**	**-71.9**	**3.2**
Medium height 1.2 m (sample point 4)				
TSS	47.3	48.5	26.1	**-20**
Fe_{tot}	40.7	30.7	19.9	1.5
Zn_{tot}	22.4	20.4	21.4	**-17.3**
Cu_{tot}	**0**	**46.9**	**-175**	**-59.4**
Medium height 0.8 m (sample point 3)				
TSS	**83.4**	64.5	68.7	**-286**
Fe_{tot}	**78.9**	57.3	23.6	**-187**
Zn_{tot}	**35.7**	**26.5**	19.4	**-107**
Cu_{tot}	**75**	**50**	**43.8**	**-106**
Medium height 0.4 m (sample point 2)				
TSS	50	43.7	**-19.7**	**-63.7**
Fe_{tot}	57.5	**-4**	**-12.7**	**-24.8**
Zn_{tot}	**39.8**	1	**-13.2**	**-23.5**
Cu_{tot}	**46.8**	**-9.3**	**-25**	**-125**

Table 6.27 Pollutant treatment efficiency of artificially prepared stormwater depending on the medium height (gravel), %; velocity of filtration 4 m/Hr; C_{TSS} = 107.5 mg/l; C_{Fe} = 2.6 mg/l; C_{Cu} = 0.034 mg/l; C_{Zn} = 0.224 mg/l

Pollutant	Efficiency of the treatment under the duration of the filtration			
	1 hr	2 hr	3 hr	4 hr
Final effluent (sample point 5)				
TSS	**94.1**	**95.3**	**94.1**	90
Fe_{tot}	**85.5**	**86.9**	**85.8**	**82.2**
Zn_{tot}	**78.5**	53.6	**75.9**	33.9
Cu_{tot}	**67.6**	**52.9**	**58.8**	**17.6**
Medium height 1.2 m (sample point 4)				
TSS	84.1	80.3	75.7	29.9
Fe_{tot}	68.8	60.6	77.8	**-5.8**
Zn_{tot}	**77.2**	33.1	24.6	25.5
Cu_{tot}	**44.1**	**26.4**	**44.1**	**-61.7**
Medium height 0.8 m (sample point 3)				
TSS	84.6	75.7	62.6	14.5
Fe_{tot}	60.7	43.9	72.9	**-16.9**
Zn_{tot}	53.6	26.4	24.6	**-5.8**
Cu_{tot}	**41.2**	**-5.8**	**17.6**	**-58.8**
Medium height 0.4 m (sample point 2)				
TSS	66.3	61.7	54.2	**-571**
Fe_{tot}	60.1	7.3	8.3	**-766**
Zn_{tot}	58.5	40.6	47.8	**-268**
Cu_{tot}	**38.2**	**-20.6**	**-35.3**	**-741**

(Table 6.27), but it then still deteriorated as with glass as particles saturated the voidage.

TSS removal throughout 3 hours of filtration showed a breakthrough after 3 hours at 0.4 m at both velocities but the system continued to achieve 80 – 90% removal across the whole filter depth.

The later run at the higher velocity and load showed a deterioration in solid removal from the very beginning (Table 6.25) for all hours and sampling points. At both of these higher velocities with glass and gravel the overall performance deteriorated as the run progressed (sample point 5).

Fig. 6.44 represents the PSD analysis for 3 glass filter runs and Fig. 6.45 the PSD for 2 filter runs using pea-gravel. On analysing the results for glass one can see that smaller and smaller particles are removed with time.

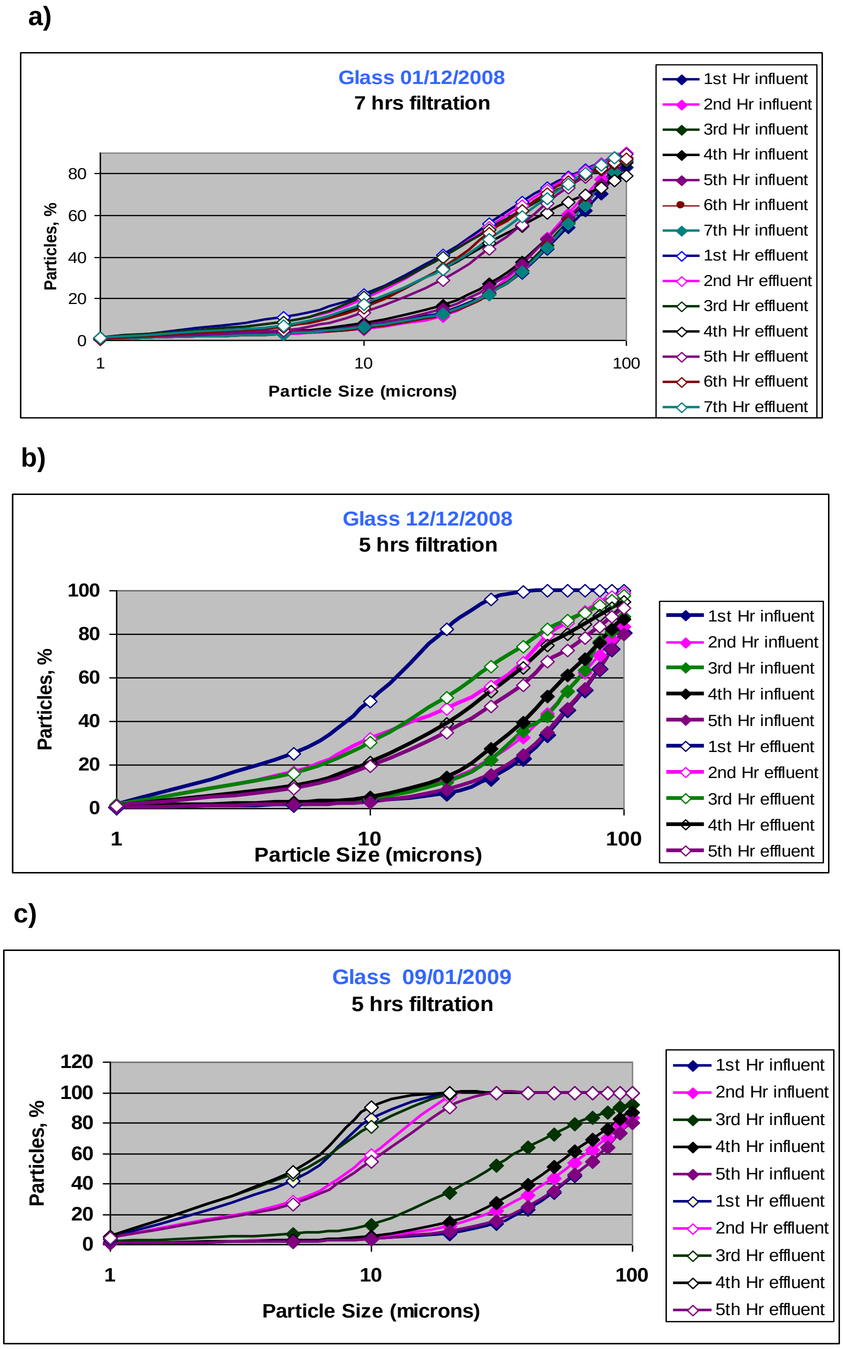
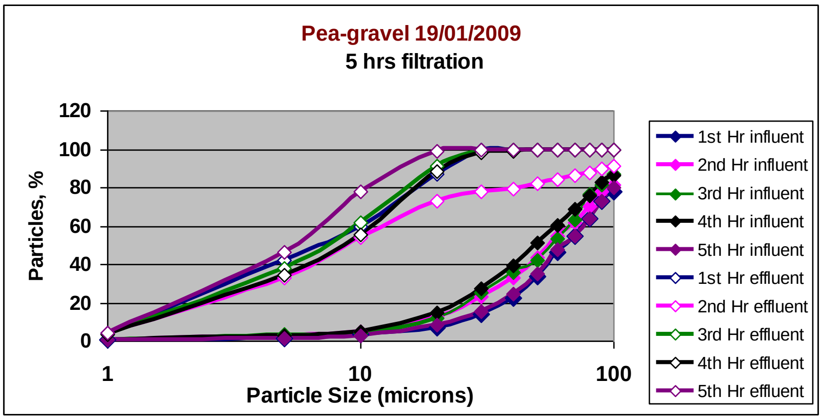


Fig. 6.44 PSD for crushed glass

a)



b)

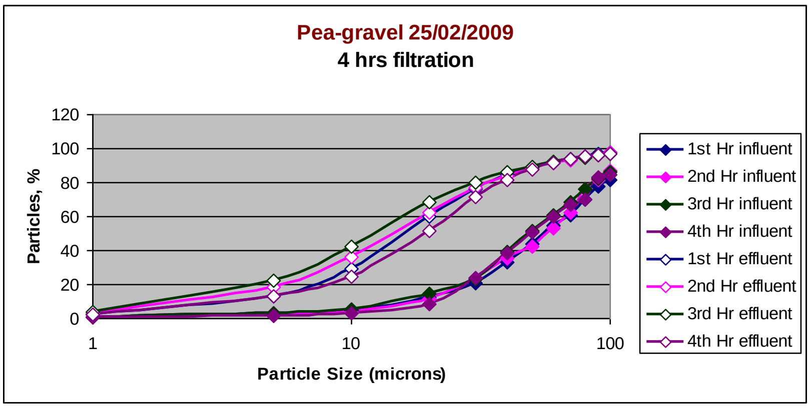


Fig. 6.45 PSD for pea-gravel

This has been summarised in Table 6.28. The last filter run of 09/01/2009 shows the best performance, as is to be expected if the enhanced particle retention is caused by the accumulating sediment layer reducing the pore size and voidage capturing smaller and smaller particles. Smaller particle capture also improves with the number of filter runs, as would be expected, if sediment accumulation is progressive with solid residues left from the previous filter runs.

On analysing the results for the pea-gravel (Fig. 6.45) and Table 6.29, one can see that the later filter run (25/02/2009) captures less smaller material with filter run time.

Table 6.28 Typical PSD of influent and final effluent using crushed glass

Size, µm	Percentage below, %			
	Influent (average)	Effluent		
		01/12/2008	**12/12/2008**	**09/01/2009**
10	5.39	17.89	30.51	72.96
20	13.16	22.55	50.58	97.2
50	44.91	68.59	80.76	100

The behaviour of the pea-gravel medium was unexpected as it was assumed that the same sediment layer would coat its surface and improve retention. The likely explanation is that because of the smaller particle size the available voidage is filled more quickly and this leads to deterioration in performance due to channelling. This is supported by the earlier data (Tables 6.26 and 6.28) which shows a more rapid accumulation of solids for gravel than for glass (see Table 6.33, comparing the surface area of gravel and glass).

Table 6.29 Typical PSD of influent and final effluent using pea-gravel

Size, µm	Percentage below, %		
	Influent (average)	Effluent	
		19/01/2009	**25/02/2009**
10	4.1	61.6	32.9
20	11.29	83.4	60.6
50	44.06	96.43	88.74

Table 6.30 presents a summary of the dissolved water quality parameters when the medium was washed. The latter was deliberately not washed immediately after each run in order to imitate ADWP. The minimum values in the flush column represent the water quality following the early filter runs and the maximum ones show the concentrations of the pollutants accumulated later into filter runs and not removed by earlier washing. The washed Fe_{dis} and Cu_{dis} concentrations increased, but not dramatically, during the 12 months of use, which confirms that there is little capacity to absorb dissolved ions. It is possible that these figures mimic the iron and copper concentrations that might have been found in the leachate from the original newly crushed glass, although these were confirmed by acid washing to be reduced to the background levels before the experiment was started. Another factor may be the increase in TOC concentrations, which acts as a chelating agent for the metals.

Crushed glass could be disadvantaged from potential use if it has a deleterious impact on water quality. Wartman et al. (2004) pointed out that the leaching of metals was a barrier to using recycled crushed glass in concrete or asphalt paving materials, although it was cheap and exhibited excellent strength and workability characteristics.

The NO_3 concentrations during the medium wash increased almost 3 times and this was the greatest increase with sodium compared to that obtained at the beginning of the filter runs. It may be explained by sediment decomposition within the column, which resulted in the release of nitrates. This level of NO_3 can be compared to that of Woodbrook during dry weather.

Table 6.30 Some water quality parameters in flushed water after a filter run

Pollutant, mg/l, except from pH and EC	Influent (range)	Column flush (range)
Fe_{dis}	0.003 – 0.006	0.008 – 0.019
Cu_{dis}	0.005 – 0.006	0.019 – 0.023
Zn_{dis}	0.021 – 0.030	0.020 – 0.030
Na	19.07 – 31.72	21.76 – 29.34
TOC	4.17 – 5.89	11.09 – 12.39
EC	450 – 490	450 – 470
TDS	250 - 330	220 – 250
pH	7.0 – 7.5	7.0 – 7.2
NO_3	14.6 – 14.8	27.18 – 34.78
PO_4 as P	0.64 – 0.68	0.716 – 0.728

Another feature of the data is that the Zn_{dis} concentrations remained the same. It was shown in the previous section 6.2.2 that Zn_{dis} concentrations might be linked to ion exchange with Na which released bound zinc from the sediment. Neither the Zn nor the Na showed a linked change.

6.6 ADSORPTION

Standard equilibrium isotherms were used to analyse and experimentally investigate potential sorption of metals onto the filtration media. Batch tests were used in this study to determine equilibrium concentrations between dissolved methylene blue (a standard adsorbate) and copper solution (shown in the work so far to be the most soluble metal) and the solid phase (recycled glass and pea-gravel adsorbent as used in filtration). The methylene blue was used in this study as the standard absorbent usually used to test activated carbon and would also be representative of organic matter present in highway runoff. The adsorption isotherm equations are characterised by constants whose values can be compared between materials, usually sand and carbon, and express the surface properties and affinity of the adsorbent. They can also be used to find the total adsorptive capacity of the media. The Langmuir and Freundlich equilibrium models are the most common equations for describing adsorption equilibrium.

The Langmuir adsorption isotherm has been successfully applied to many pollutants (McKay et al., 1985; King et al., 2007) and has been the most widely used sorption isotherm. The basis of the Langmuir theory is that sorption takes place at specific homogeneous sites on the adsorbent and the saturated monolayer isotherm can be expressed in its linearised form by:

$$\frac{C_{eq}}{{}^{X}\!/_{m}} = \frac{1}{K_L b} + \frac{1}{b} C_{eq} \qquad (6.4)$$

where X/m is the adsorption density, mg/g; C_{eq} is the concentration of adsorbate in solution at equilibrium, mg/l; b is the adsorption capacity corresponding to complete monolayer coverage, mg/g; K_L is the Langmuir constant related to the energy of adsorption, L/mg.

The linear behaviour of $\frac{C_{eq}}{{}^{X}\!/_{m}}$ versus C_{eq} yields the Langmuir constants b and K_L.

The alternative Freundlich model is an empirical isotherm and can be used for non-homogenous sorption and expressed by the following equation:

$$C_{eq} = K_F C_{eq}^{1/n} \qquad (6.5)$$

where K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the sorbent, respectively.

It is important to note that the sorption isotherms do not provide any information about the mechanism of sorption, which has to be confirmed by more direct methods based on molecular spectroscopy.

Nevertheless, the isotherms have been classified into four adsorption rate patterns, according to their shape, and linked to mechanisms (McBride, 1994):

1) the *L-type* (logarithmic) (classic Langmuir) isotherm reflects a relatively high affinity between the adsorbate and adsorbent (chemisorption);

2) the *S-type* isotherm (power), suggesting “cooperative adsorption”, operates if inter-molecular attraction within the adsorbate-adsorbate interactions is stronger than the adsorbate-adsorbent interaction. In this case adsorbate molecules bond more strongly with one another than with adsorbent (surface);

3) the *C-type* (linear) (constant-partitioning) isotherm, suggesting a constant relative affinity of the adsorbate molecules for the adsorbent, is normally observed at the low range of adsorption;

4) the *H-type* isotherm is a very strong adsorbate-adsorbent interaction and a more likely pattern than the ideal model and extreme case of the I-type adsorption.

The adsorption isotherms obtained in this study (Fig. 6.46) can be related to the *C-type*, being found at low concentrations.

Fig. 6.46 (a; b) represents sorption isotherms for two types of crushed glass (blue and transparent) and pea-gravel.

a)

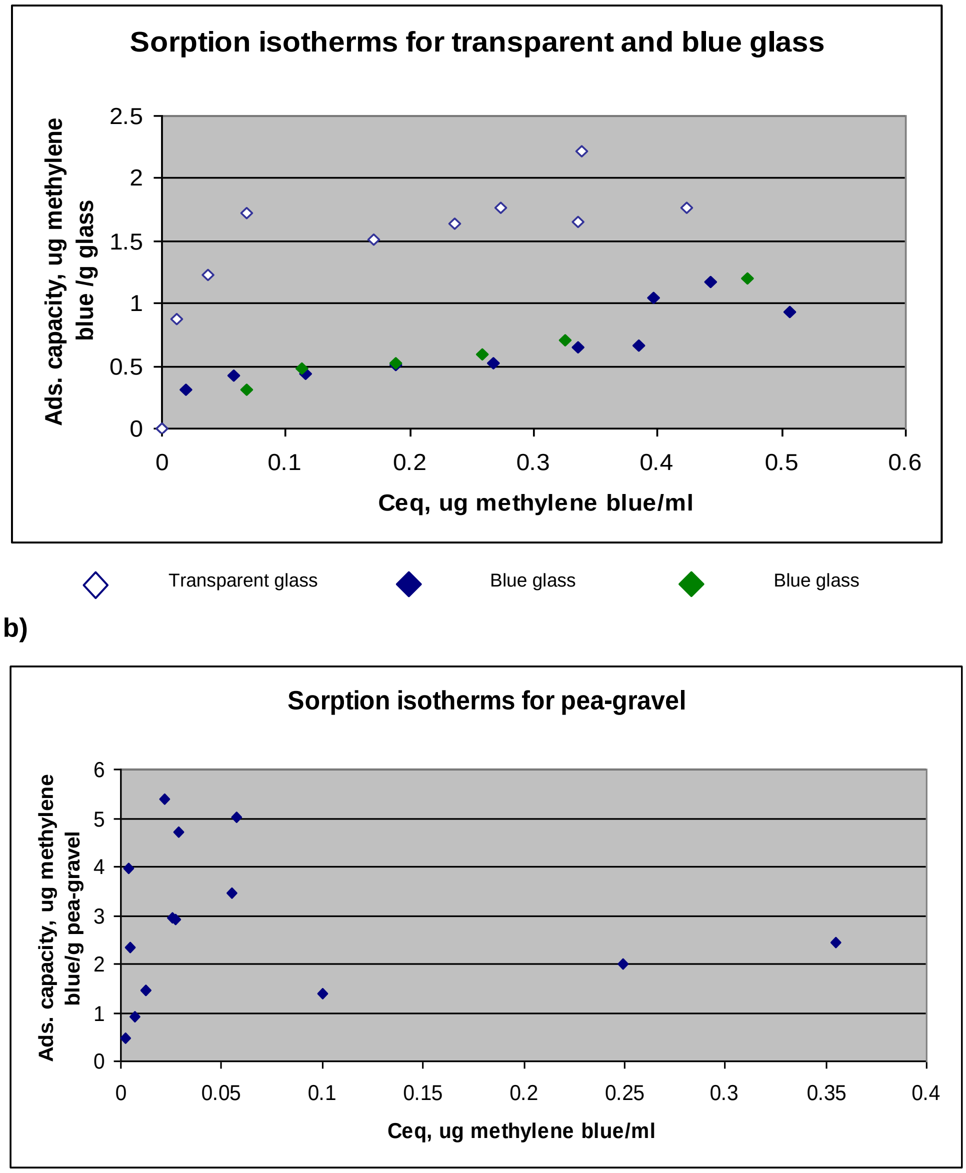


Fig. 6.46 Sorption isotherms for crushed glass and pea gravel

Fig. 6.46 a shows 2 equilibrium plots for blue glass and 1 for transparent glass. Fig. 6.46 b represents 2 experiments for pea-gravel. The initial concentration of adsorbate (methylene blue) in each batch flask ranged from 0.05 to 0.6 mg/l with a fixed mass of adsorbent in all cases of 5 g. Each experimental point was obtained based on the colorimetric absorbance value (see section 5.4, Methodology) and then the C_i and *adsorption capacity* were calculated for each period of time.

Table 6.31 shows, as an example, a summary of one of the data sets selected for discussion for both blue crushed glass and pea-gravel with an initial concentration of methylene blue of $C_{initial}$ = 0.24 mg/l.

Table 6.31 Experimental and calculated sorption results

	Sorbent		M = 5.00 g; V = 50 ml; C_{initial} =0.24 mg/l; Initial absorbance = 0.466				
Period of time		1 Hr	2 Hrs	3 Hrs	22 Hrs	24 Hrs	32 Hrs
Absorbance	**glass**	0.409	0.368	**0.364**	**0.372**	0.357	0.384
	pea-gravel	0.225	0.137	0.106	**0.025**	***0.03***	0.033
C_i **, mg/l**	**glass**	0.2074	0.1899	**0.1879**	**0.1919**	0.1844	n/a
	pea-gravel	0.1182	0.0740	0.0585	**0.0178**	**0.0204**	n/a
Adsorption capacity, mg/mg	**glass**	3x10^{-7}	5x10^{-7}	**5.21x10^{-7}**	n/a	n/a	n/a
	pea-gravel	1.2x10^{-6}	1.6x10^{-6}	1.815x10^{-6}	**2.222x10^{-6}**	n/a	n/a
Effectiveness (mass absorbed), %	**glass**	13.6	20.9	21.7	n/a	n/a	n/a
	pea-gravel	50.8	69.2	75.6	92.6	n/a	n/a

n/a – not applicable

The bold blue data indicate equilibrium concentration for crushed glass and the bold brown show that for pea-gravel. From the Table it can be seen that blue crushed glass achieved the equilibrium concentration in 3 hours, whereas pea-gravel took 22 hours. Normally the equilibrium concentration for gravel was achieved within 22 – 24 hours, but in some cases it was prolonged up to 148 hours (more cracks). The suggestion is that this supports the evidence for the transport being rate limiting. Other work (Davies and Wheatley, 2010) has shown that gravel has a number of small < 1 – 2 μm cracks and this could delay equilibrium. The surface of glass does not show this. When the initial concentration of the methylene blue was increased, the equilibrium concentration for glass was achieved faster (within 1 – 2 hours), suggesting mass transport limitations although the flasks were mixed. Looking at Fig. 6.46 b, one can see that the pea-gravel adsorption capacity was higher than that of crushed glass (all types), but the behaviour of glass was less variable.

Fig. 6.47 shows a second data set indicating the depletion of methylene blue ($C_{initial}$ = 0.6 mg/l) from solution by both different types of crushed glass and pea-gravel.

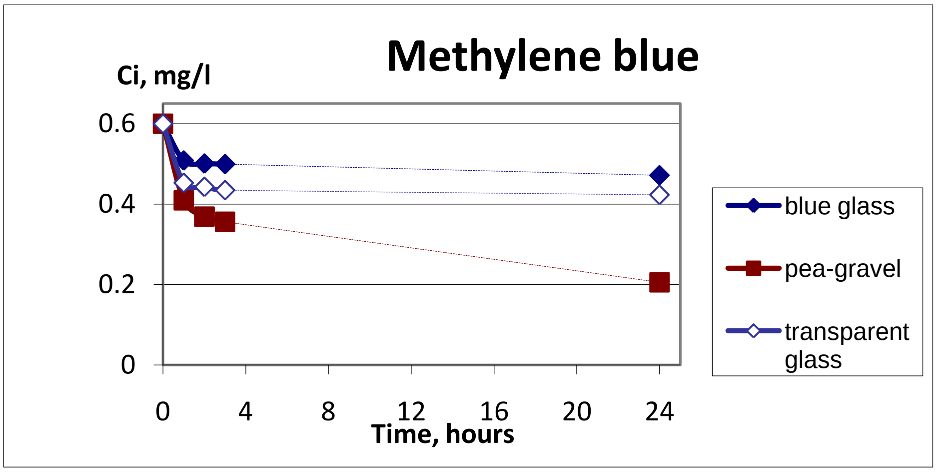


Fig. 6.47 Depletion of methylene blue

It can also be concluded that the uptake of the methylene blue (amount and rate) was greater by pea-gravel, which lends support to the theory of a greater surface area.

Table 6.32 summarises typical data as in Fig 6.46, but from duplicate experiments, where the mean and range values of both adsorption capacity and aqueous phase equilibrium concentration were taken. For pea-gravel the values of short-term adsorption were excluded (3 points).

Table 6.32 Equations for obtaining adsorption capacity

Type of adsorbent	Equation	R^2
Blue glass 5 gr	Y=1.7059x+0.226	0.845
Transparent glass 5 gr	Y=3.003x+0.9689	0.6463
Pea-gravel 5 gr	Y=14.27x+1.287	0.7746

Despite the fact that methylene blue is a standard adsorbate for analysis and test work which has been investigated by a number of studies, many of these studies have been comparisons of adsorption capacity with activated carbon, hence, most previous research has concentrated on investigating the properties of activated carbon (Shimada et al., 1999; Jaguaribe et al., 2005). Much greater levels of adsorption capacity are reported because the specific surface areas are greater (see Table 3.1).

Table 6.33, which reports the surface area results for glass and gravel, shows that glass has a lower surface area in comparison with gravel. One can see that the values have wide fluctuations, which might be explained as resulting from the presence of different cracks and crevice structures in the surface of the material. No information was found about crushed glass being used as an adsorbent, although it has been used as a filter medium.

Table 6.33 Surface area results

Sample No.	Area, m^2/g
Pea gravel semi-crushed (5-10 mm)	2.119
Pea gravel semi-crushed (5-10 mm)	14.719
Crushed glass (blue)	1.374
Crushed glass (blue)	0.635
Natural semi-crushed gravel (10-20mm)	2.977
Natural semi-crushed gravel (10-20mm)	0.378
Activated carbon	1000

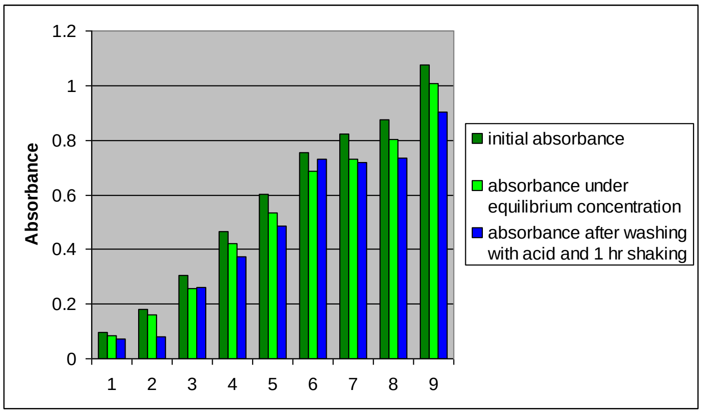
The results shown in Table 6.33 suggest that surface area is a parameter that will affect possible adsorption at natural pH's but it was also possible that the greater adsorption potential of gravel was attributable to the greater ionisation of the Ca compared to silica.

Other materials have also been studied and a selected example to represent natural organic matter in the environment was published by Han et al. (2007). They studied the removal of methylene blue by leaf compost (*Phoenix dactylifera)* to find a more sustainable alternative to activated carbon with a lower running cost. The procedure of sorption tests used in their study was similar to ours, but the initial concentration of the methylene blue (MB) was 70 mg/l compared to our 0.6 mg/l. These higher concentrations are unrealistic as representative of highway drainage.

Bestani et al. (2008) also studied the sorption characteristics of the leaves of a desert plant called *Salsola Vermuculata* using methylene blue and they found an impact of pH. It was observed that there was a decrease in the methylene blue uptake at lower pH values, probably due to competition from the protons with the dye molecules for the available adsorption sites. With increasing pH, the adsorbent becomes negatively charged which results in an enhanced attraction between the positively-charged dye molecules and the adsorbents' surface. This possibility was investigated for glass and gravel in our work.

In order to determine whether the adsorption of the methylene blue resulted from either physical or chemical interaction with the surface (Fig.6.48), a second experiment was run under acid conditions. 10% of HNO_3 was added to samples and shaken for 1 hour.

a) 1gr of blue glass



b) 5gr of transparent glass

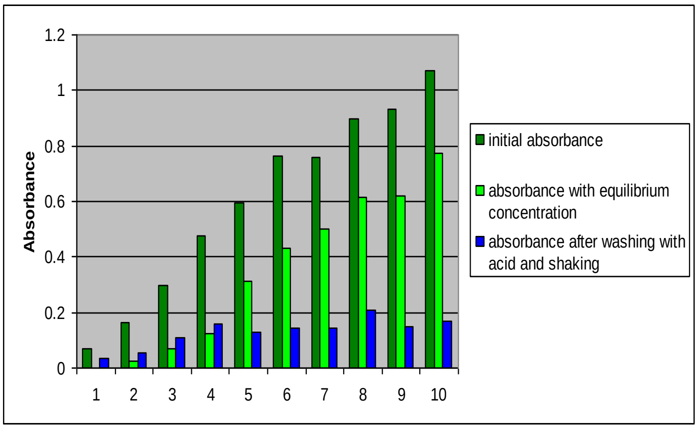


Fig. 6.48 Adsorption of methylene blue by two types of glass

The adsorption to the transparent glass is enhanced by the acidic conditions and shows a surprising difference between the surface chemistry of blue and transparent glass.

Under acid conditions the MB is totally ionised and adsorption would mainly be through chemical or electrostatic adsorption.

The same experiment was attempted with pea-gravel but after HNO_3 was added, the gravel was dissolved, which could have been anticipated from these low pH values and can be described by the formation of soluble calcium nitrate:

$CaCO_3 + 2\ HNO_3 = H_2O + CO_2 + Ca(NO_3)_2$

Fig. 6.49 shows the adsorption of Cu from blue crushed glass and pea-gravel, the alternative ionised tracer to model adsorption and at the two different pH values of 6.5 and 9.5 to change the ionisation potential of copper.

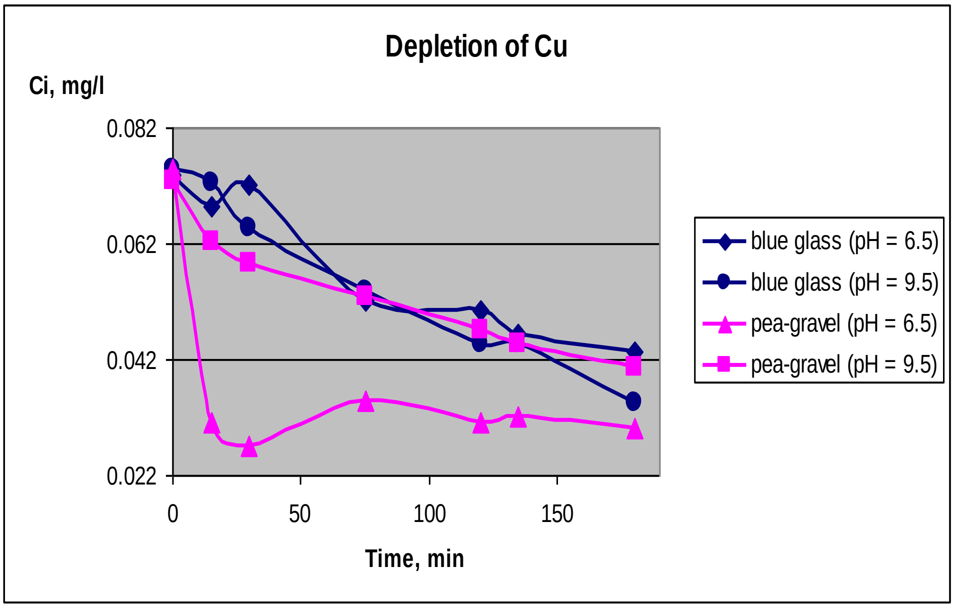


Fig. 6.49 Depletion of copper

Conditions: adsorbate – copper; adsorbent – recycled blue crushed glass and pea-gravel; V = 100 ml.

Table 6.34 summarises the statistics for the data shown in the graphs above (Fig. 6.49) after 24 hours.

Table 6.34 Depletion of copper after 24 hours by blue glass and pea-gravel

$Cu_{initial}/Cu_{24hours}$, mg/l			
Blue glass		Pea-gravel	
pH = 6.5	pH = 9.5	pH = 6.5	pH = 9.5
0.074/0.063	0.075/0.024	0.075/0.008	0.073/0.016

The pH is therefore a crucial parameter affecting the uptake. The best performance was shown by pea-gravel at acidic pH = 6.5. Within the first 15 minutes the Cu concentration decreased sharply from 0.075 to 0.031 mg/l and continued decreasing slowly for another 15 minutes from 0.031 to 0.027 mg/l, which was its equilibrium concentration. The uptake of copper was linear at pH=9.5, and similar to the glass (Fig. 6.49) but the absorbance was half that at pH =6.5. One can see that the decrease was linear with time, without any fluctuations (Fig. 6.49). Keskinkan et al. (2004), studied metal removal, including that of Cu, by biosorption using an aquatic submerged plant called *Ceratophyllum demersum* (coontail or hornwort), which is typical of treatment lagoon/ponds, and they showed that a contact time of 20 minutes was sufficient to achieve equilibrium concentration. Maximum adsorption capacity for the plant was 6.17 mg/gr for Cu(II) with an initial concentration of copper of 10 mg/l, which was more than 100 times higher than the concentration used in this study to represent highway runoff. This higher concentration may have avoided some of the solubilisation effects. The adsorption capacity obtained both for crushed glass and pea-gravel is summarized in Table 6.35.

Table 6.35 Adsorption capacity of crushed glass and pea-gravel

Adsorption capacity, µg of copper/g adsorbent				
Glass		Pea-gravel		
pH = 6.5	pH = 9.5	pH = 6.5	pH = 9.5	Keskinkan et al. (2004) (pH= 5.9)
0.102 (15 min)	1.02 (24 hours)	0.96 (15 minutes)	1.34 (24 hours)	6, 170

Keskinkan et al. (2004), working on leaf compost, noted that pH values just below 6 were suitable for metal adsorption, promoting ionization of the metal. Their results, however, did not include comparative experiments for different pH values.

This suggests that the acid environment does assist the speed of metal binding possibly by increasing the ionisation of the metal, as suggested by Keskinkan et al. (2004), and promoting ionic binding but also possibly by ion exchange. With an increase in pH from 6.5 to 9.5 Cu a standard linear uptake was observed with a better ultimate decrease of the Cu concentration from 0.075 mg/l to 0.035 mg/l in (180 min). In the cases of both glass and pea-gravel at pH=9.5 the equilibrium concentration was not achieved within 24 hours. It was concluded that adsorption was physical and therefore much slower. Another feature of this data is that the EQS for Cu_{dis} (0.01 mg/l) was achieved only for the pea-gravel with a pH value of 6.5 after 24 hours (0.008 mg/l) (from an initial concentration of 0.075 mg/l or 0.1 mg/l).

The Cu removal using crushed glass showed the same linear pattern as pea-gravel, although not at pH = 6.5. The equilibrium concentration for pH=6.5 was achieved within 15 minutes and was 0.069 mg/l, showing only 7% of the copper removal, which suggested that ion exchange and co-adsorption was more important than simple ionization of the metal as suggested by Keskinkan et al. (2004). Glass was non-ionizing and not as effective for dissolved Cu removal in the natural environment.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

Analytical methods

The methods used for metal recovery were shown to play a significant role in a good correlation between metals, their standards and other water quality parameters. Comparing the two digestion methods, it was evident that microwave digestion gave better recovery of total metals than hot plate digestion, which affected the results of the metal partition. The microwave aqua regia digestion increased elemental recovery for iron, copper and zinc. It was concluded that microwave digestion prevented some metal volatilisation. This explained why copper and zinc in our study were found mostly in the attached form compared to previous studies, where they were mostly dissolved.

M1

Pollutant concentrations (metals, solids and other common parameters [see section 6.2]) in the runoff from a major highway were shown to depend on many factors but season was the main one. Evaporation during a prolonged dry period increased total Fe by 150 % and total Zn by 60 %. De-icer salts in the lagoon washed off from the road junction increased dissolved zinc by 400 % and these were the strongest influences on pollutant concentrations entering the catchment.
Storm characteristics (rainfall intensity and duration) were also important but secondary to ADWP and cold weather. The prolonged dry period may increase concentrations of pollutants in the lagoon both due to evaporation but also ion exchange from the sediments. There was evidence that Fe_{dis}, for example, increased due to dry weather because of both evaporation and re-solubilisation from the sediment. Further work is needed on well controlled redox experiments with sediments to confirm this. Prolonged rains, on the other hand, cause a diluting effect of the pollutants from the M1.

It was concluded that evaporation and consequently pollutant concentrations depend on ADWP and temperature. The influence of de-icer salts and their concentration depended on the duration of sub-zero temperatures.

ADWP and rainfall intensity were confirmed as important influences on producing a first flush which increased pollution concentration in the runoff. However, local conditions of the catchment can confound these simple results.

Metal concentrations in the runoff from the M1 varied widely according to these weather conditions. The variability in weather conditions and long-term trends affect the statistical reliability of the results and continued work will always be needed to further adjust the means and range of values published in this thesis.

Similar variance was, however, found in the natural rural brooks in the catchment. There was much less variability in the metals from the treated sewage effluents entering the catchment. This was attributed to the flow buffering and complexity of sewage treatment.

Further work is recommended to study long dry periods, providing information on the potential bioavailability and mobility of metals between the water, biomass and bottom sediment (adsorption and desorption) under the influence of storm characteristics, temperature and de-icer shocks.

Fe was always at the highest concentrations for all weather conditions, total and dissolved, and in all sampling locations (Fe_{tot} was 1.119 mg/l and Fe_{dis} was 0.103 mg/l for dry weather in the lagoon sampling point; and for wet weather Fe_{tot} was 2.104 and Fe_{dis} was 0.127 mg/l).

Cu concentrations varied even more widely and were in the lowest concentrations of the metals and showed the greatest solubility on average. The maximum value of Cu_{dis} found in the inlet during wet weather was 0.042 mg/l with an average hardness of 175 mg/l, which exceeded the EQS for Cu_{dis}, (0.01 mg/l) but this was still lower than the results from previous work. It was concluded that this was because copper is generated while the vehicles are braking but the M1 has continuously moving traffic. The second reason for this is that the samples were not filtered and preserved immediately on the site, which might have resulted in insoluble complex formation.

It was found that while analysing metals in runoff, the results obtained from grab samples are likely to be both more reliable and reproducible, since it is assumed that metals will be analysed as soon as possible, although it is more laborious. It is recommended that sample aging/deterioration be investigated, including the preservation of samples taken automatically.

Zn_{tot} concentrations in the M1 run off exceeded the EQS (0.075 mg/l) during wet weather (0.141 mg/l on average). During dry weather they were 3 times lower, but still higher compared to the rural brooks. Throughout the period of this study we did not observe any exceedence of concentrations on average for any metal in the lagoon. However, in some cases (prolonged dry weather period) increased Zn_{tot} concentrations (0.215 mg/l) were found because of evaporation. It is suggested that further work is needed to understand the reasons for differentiating Zn from the other metals by defining the EQS of Zn in total.

The behaviour of metals in terms of their solubility was shown to be metal - dependant. Thus, Zn solubility was found to be increased by the presence of de-icer salts which releases them from the sediment by an ion-exchange mechanism suggested by the literature. A similar process was induced artificially in laboratory column experiments in support of the field study.
The results suggest that the solubility of Fe is increased anaerobically by reduction with organic matter to release more soluble ferrous salts.

The data show the existence of a correlation between the metals in their total form and TSS in the following sequence (Fe = 0.853; Zn = 0.794; Cu = 0.538). The correlation deteriorated if all the data were added together from different parts of the catchment area (M1 and Woodbrook) (Fe = 0.829; Zn = 0.152; Cu = 0.095). Apart from iron, the links between total metals and particles in the natural streams and sewage effluents were not apparent, suggesting the importance of the source of the metals and the nature of the TSS.

The combination of what has been adopted as standard treatment for sensitive areas and highly trafficked roads, that is interceptor and SUDS (lagoon in this case), always achieved the EU EQS for metals. It is recommended that the design criteria used for determining the size of treatment capacity be reviewed and compared with other available SUDS design guides.

Total metals were removed with TSS in the interceptor in most cases, whereas dissolved metals were not. The data of PSD shows that the interceptor did not always cope with smaller particle separation (< 25 μm) at the higher flows.

Further work is also suggested by the results on the need to make improvements to interceptors including a greater understanding of their maintenance. This may be necessary to meet future water quality requirements. Example design changes could be a cascade of chambers or additional filters, despite poor reproducibility in our filter experiments. Maintenance possibilities including regular de-sludging or inspection should be included in the design guide.

Sewage works

Each of the 3 different sewage works sampled contributed different concentrations of metals to the receiving water according to the dilution available but iron was always in the highest concentrations.

No correlations were found between metals in their soluble form and TOC or total metals and TSS. The range of TOC was between 4.6 to 8.29 mg/l and TSS from 10 to 20 mg/l.

Surprisingly few recent papers were found that analysed the metals in sewage work discharges and it is suggested that further research using EA public register might give greater statistical confidence.

The results from Osgathorpe sewage work discharge showed that Zn in its total and dissolved forms and dissolved Fe behaved conservatively (when a mass balance with flow was applied): Fe_{dis} varied with an error of 14.3%; and Zn with errors of 9.5% and 5.06%, total and dissolved respectively, between measured and predicted concentrations in the brook. The worst and the most erratic behaviour demonstrated was that of Cu in all forms. The differences between measured and predicted values were: Cu_{tot} – 87.5% and for Cu_{dis} – 140%. The discrepancy between measured and predicted concentrations can be explained by the more complex speciation behaviour – it is not conserved.

During dry weather metal concentrations in the receiving water were increased by sewage work effluents, but not during wet weather when the concentrations were diluted. More work is needed to exclude the bias of flow rate, upstream water quality and stream morphology to draw conclusions about the environmental effects. The concentrations of metals in the effluents were always below the EQS.

Woodbrook

As with the other sampling sites Fe was always at the highest concentrations for all weather conditions and species, probably as it is the most ubiquitous element in the soil. There is also still the possibility of a contribution from the iron land drains. The recorded concentration of Fe during dry weather in its total and dissolved form (Fe_{tot}/Fe_{dis}) was 0.192/0.046 mg/l and for wet weather it was 2.65/0.167mg/l. Fe solubility was small (6.3% during wet weather and 23.9% during dry weather), indicating that most of the Fe is affiliated with particulate matter.

The results of Fe_{tot} in the M1 lagoon during dry weather were greater (10 times higher – 1.119 mg/l). It was concluded that this was due to the continuous flow in the brook, whereas the lagoon was stagnant. This increased TSS both as a result of algal growth and evaporation. The equivalent wet weather concentration from the M1 was 2.104 mg/l for Fe_{tot} and 0.127 mg/l for Fe_{dis}. The average Fe concentrations in the sewage work effluent, which were not differentiated by dry and wet weather, were 0.089 mg/l for Fe_{tot} and 0.05 mg/l for Fe_{dis}.

Zn was mostly found in its dissolved form, like the sewage effluent but unlike the M1 where more Zn was attached to solids, as noted previously. The concentrations of Zn during dry weather in its total and dissolved form (Zn_{tot}/Zn_{dis}) were 0.035/0.005 mg/l and for wet weather it was 0.079/0.025 mg/l. During wet weather Zn_{tot} exceeded the EQS. The similar concentrations for the M1 for wet weather were 0.141 mg/l for Zn_{tot} and 0.037 mg/l for Zn_{dis} and for the sewage works the average concentrations were 0.057 mg/l for Zn_{tot} and 0.048 mg/l for Zn_{dis}.

Copper showed the strongest association, with fractions less than 0.45 um, compared to Fe and Zn. This was similar to the results from the M1 and in sewage effluent. The dissolved fraction of Fe and Zn increased in the brooks after the application of de-icer salts to the roads, but the solubility of Cu remained the same. Wet weather generated increased concentrations of all the indicator metals: Zn_{tot} = 0.202 mg/l (15/04/2009). EQS for Zn_{tot} = 0.075 mg/l for hardness from 200 to 250 mg/l. Cu_{dis} = 0.022 mg/l (15/01/2008), EQS for Cu_{dis} = 0.01 mg/l for hardness from 200 to 250 mg/l.

Further work on other indicators such as biodiversity and sediment metal concentration could be used to determine if there was an actual environmental impact during wet or cold weather.

Metal removal by filtration and adsorption

Research to improve and intensify stormwater treatment made use of filtration and adsorption. Adsorption studies with recycled glass and standard pea-gravel indicated that gravel could remove soluble copper (the most soluble metal), particularly in acid conditions**.** It was concluded that this was due to an ion-exchange mechanism rather than enhanced ionisation of the copper. Other materials such as recycled demolition waste might be better and should be investigated.

Column filtration studies to improve on the small particle capture shown by the interceptor used gravel and recycled glass. Filtration was able to remove particles down to 5 µm but at a typical flow rate (5 m/hr) and solid loading it was concluded that the filters would, as with other water filters, need washing after every major storm. It is recommended the research be extended to include larger filter media than normal for natural waters to allow for the greater accumulation and turnover of solids.

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Appendix 1

Monthly amount of precipitation for 2007, 2008 and 2009

Monthly amount of precipitation for 2007 (Leicester Weather Station) (http:// www.stormtrack.co.uk/)

Day	January	February	March	April	May	June	July	August	September	October	November	December
1	No data						7.4		0.2			0.4
2							2.6		0.8			4.6
3						11.8	7.0					1.6
4			9.8				4.2			0.2		
5		0.4	0.8				5.0				0.2	
6							5.2					
7			0.2		1.4							
8		0.4					4.4				2.0	
9		4.4					0.4			9.6		
10		5.2								0.4	0.2	0.4
11					7.2					0.2		
12		1.4			6.8		0.6					
13		0.8			11.4	1.0	3.0				1.8	0.2
14		0.2			2.2	23.0	1.0	6.6			0.2	
15					3.2	3.8	1.4	3.2				
16		5.8			3.6		4.4	0.2	0.4	0.4		
17					2.2	3.6	8.2		3.8		0.2	0.2
18							0.4	4.8			14.2	
19		0.6			0.2	5.4		11.8	0.6		7.0	
20		0.2				0.2	17.2	0.4	1.2		2.6	
21		1.0				5.6	10.2		2.0		0.2	
22		3.2				15.0					0.8	1.0
23		5.0	0.6	0.2			1.0		0.2			0.2
24		3.6				0.6	0.2		7.4	0.2	0.4	2.0
25		0.8			0.4	0.6	1.2		4.6			4.0
26		0.2				7.0	23.4				0.2	0.2
27				0.8	11.6	3.6	0.2		0.2	0.4		
28					10.2		2.0		1.2	1.0	0.2	1.6
29							1.4		0.6	0.2	0.2	1.8
30					2.0						2.8	
31												
Total:		**33.2**	**11.4**	**1.0**	**62.4**	**81.2**	**112.0**	**27.0**	**23.2**	**12.6**	**33.2**	**18.2**

Monthly amount of precipitation for 2008 (Leicester Weather Station) (http:// www.stormtrack.co.uk/)

Day	January	February	March	April	May	June	July	August	September	October	November	December
1		0.4	1.0	1.2	0.4	0.4		5.8	10.4	2.8	16.0	
2	0.2		0.2	0.2	0.6	1.0	0.2	10.8	7.0	0.4	4.2	1.0
3		0.2	0.2			20.4	2.4		4.0	0.2	0.2	0.4
4	2.2	7.2			0.6	0.2			2.0	4.0	1.0	5.6
5		10.6		4.8	1.6		5.2	1.8	22.2	27.0	1.8	0.4
6	1.8	1.6				0.6	4.8		13.4		0.6	
7	2.0		0.4			0.4	4.6	0.4	3.4	1.4	0.8	0.2
8	2.6		1.4					1.4	0.2		15.6	6.4
9	0.2		0.6	0.2				5.6	7.2		13.4	0.2
10	0.6	0.2	7.8	0.2			10.4	0.8	0.2		3.6	
11	14.0		6.4	2.8			0.2	0.4	0.2		2.0	
12	1.0		0.2	2.4		1.8		13.2	2.4			0.6
13	0.2	0.2	0.2					1.2	0.2		1.6	12.0
14	1.2	0.2	0.2	2.4				0.4	0.2	0.2		1.0
15	16.2		8.0	3.0						1.6	0.8	
16			8.2	0.8	1.4	0.8	2.2			1.0		1.4
17	8.4						0.2	13.8	0.2		0.8	
18	5.6	0.2				1.2	2.2	1.6			0.6	2.2
19	3.4					1.2		1.8			0.2	
20	4.4		0.2	2.0				2.6		3.6		3.4
21	4.4		1.6			3.0		3.2				0.2
22	0.2		1.4			2.6		0.8	1.6			
23			1.0	0.4	0.2				0.4	1.2	1.6	
24	0.4	0.4		2.8				4.2	0.2	1.0	0.6	
25		0.2	0.4		2.4					0.2		
26		2.6	4.8		2.4	1.6				6.8		
27			0.2	11.2	7.0	0.2				0.2	2.4	
28			3.2	1.2	15.2	0.6	3.4			2.8		
29	1.6	2.6	1.4	7.6	7.6	3.6				0.2	0.2	
30	0.2			4.4	0.8		1.0		1.8	3.6		
31	2.4		0.2					2.8		0.2		
Total:	**73.2**	**26.6**	**49.2**	**47.6**	**40.2**	**39.6**	**36.8**	**72.6**	**77.2**	**58.4**	**68.0**	**35.0**

Monthly amount of precipitation for 2009 (Leicester Weather Station) (http:// www.stormtrack.co.uk/)

Day	January	February	March	April	May	June	July	August	September	October	November	December
1							0.2	9.0	4.2		14.6	2.2
2	0.2	1.6							14.6		0.2	1.6
3		4.0	7.0		0.2		12.0		3.2		7.2	1.6
4		2.0			0.8			4.4		0.2	2.0	2.0
5	1.8	2.4			0.6	3.8	0.2	10.6			0.2	6.0
6		2.4				10.6	14.4	12.0	0.2	2.6	1.0	6.8
7	1.2	1.6	0.2		0.2	13.6	6.2	8.2		11.0		1.8
8	0.4	0.4	2.6	1.4	1.2		1.2		0.2		0.4	1.4
9		7.0		1.0						1.4	0.2	2.2
10		3.4		2.0		0.2		1.0			0.6	0.2
11	0.2	0.8		0.2		0.4	3.8				1.0	0.2
12	8.8	2.2		0.2			2.8	3.2			7.2	0.2
13	0.2	1.4			0.2						4.0	1.4
14	0.2			0.2	0.2		3.0				2.6	3.0
15	0.2			3.8	13.8	23.4	1.2			1.8	0.4	0.2
16	0.4			0.8	1.6		6.0			0.4	3.2	3.2
17	10.6			0.4	2.0	1.2	23.4				0.2	0.2
18	1.4	2.4			0.2					0.2	1.2	
19	4.8	0.2	0.2		1.8		6.8					0.2
20		0.2			2.2	0.8				2.0	1.2	
21	1.0				0.6		7.6	3.4		1.0	4.4	0.2
22	4.0										0.6	
23	4.4		1.2				1.6				2.8	3.0
24	0.4		0.4				8.0			1.2	1.8	0.4
25	0.8		1.6		0.2		0.2	0.6			4.2	0.8
26					1.0	0.6	4.0	3.0			0.2	0.2
27	0.6		0.2	9.8	0.6	0.6	2.4	0.6		0.8		0.4
28	6.2		0.6	3.8				2.6			4.6	
29	0.2						22.2				2.8	4.6
30				3.6			4.8	1.2		0.2	1.6	5.6
31							0.4			1.4		
Total:	**48.0**	**32.0**	**14.0**	**27.2**	**27.4**	**55.2**	**132.4**	**59.8**	**22.4**	**24.2**	**70.4**	**49.6**

Appendix 2

Environmental Quality Standards for some metals, EC Dangerous Substances Directive (76/464/EEC)

http://ec.europa.eu/environment/water/waterdangersub/pdf/article7ofdirective77464eec.pdf (14/12/2010)

Metal	EQS type	All freshwater, µg/l (depending on hardness, mg/l $CaCO_3$)						Coastal and estuarine, µg/l
		0 – 50	50 – 100	100 – 150	150 – 200	200 – 250	>250	
Freshwaters, suitable for all fishlife								
Copper (dissolved)	Annual average	1	6	10	10	10	28	5
Copper (dissolved)	95th percentile	5	22	40	40	40	112	
Freshwaters, suitable for Salmonid (game) fish								
Zinc (total)	Annual average	8	50	75	75	75	125	40
Zinc (total)	95th percentile	30	200	300	300	300	500	
Freshwaters, suitable for Cyprind (coarse) fish								
Zinc (total)	Annual average	75	175	250	250	250	500	
Zinc (total)	95th percentile	300	700	1000	1000	1000	2000	
Iron (dissolved)	Annual average	1000 (not related to hardness)						1000

Appendix 3

Erratic data from the flow meter

Flow meter recordings for 13/11/09, 21/11/09 and 07/12/09

Erratic data from the flow meter

Starflow ultrasonic doppler
flow recorder models A
S/N: 4375

Time	Depth (AVG) mm	Velocity (AVG) mm/s	Temperature (AVG) Deg C	Battery (RAW) V	Flow Rate(AVG) l/s
27-08-09 12:15:00	68	0	19.05	12.58	0
27-08-09 12:30:00	68	0	19.07	12.58	0
27-08-09 12:45:00	67	0	19.1	12.58	0
27-08-09 13:00:00	67	0	19.1	12.58	0
27-08-09 13:15:00	67	0	19.14	12.58	0
27-08-09 13:30:00	67	0	19.16	12.58	0
27-08-09 13:45:00	67	0	19.18	12.58	0
27-08-09 14:00:00	67	0	19.27	12.58	0
27-08-09 14:15:00	66	0	19.35	12.58	0
27-08-09 14:30:00	66	0	19.41	12.58	0
27-08-09 14:45:00	66	0	19.42	12.58	0
27-08-09 15:00:00	66	0	19.41	12.58	0
27-08-09 15:15:00	66	0	19.37	12.58	0
27-08-09 15:30:00	66	0	19.32	12.58	0
27-08-09 15:45:00	66	0	19.25	12.58	0
27-08-09 16:00:00	65	0	19.18	12.58	0
27-08-09 16:15:00	65	0	19.13	12.58	0
27-08-09 16:30:00	65	0	19.02	12.58	0
27-08-09 16:45:00	65	0	18.91	12.58	0
27-08-09 17:00:00	65	0	18.78	12.58	0
27-08-09 17:15:00	65	0	18.68	12.58	0
27-08-09 17:30:00	65	0	18.59	12.58	0
27-08-09 17:45:00	65	0	18.48	12.58	0
27-08-09 18:00:00	65	0	18.39	12.58	0
27-08-09 18:15:00	65	0	18.29	12.58	0
27-08-09 18:30:00	66	0	18.21	12.58	0
27-08-09 18:45:00	64	0	18.11	12.55	0
27-08-09 19:00:00	64	0	17.97	12.58	0
27-08-09 19:15:00	63	0	17.87	12.55	0
27-08-09 19:30:00	62	0	17.79	12.55	0
27-08-09 19:45:00	61	0	17.7	12.55	0
27-08-09 20:00:00	62	0	17.58	12.55	0
27-08-09 20:15:00	61	0	17.45	12.55	0
27-08-09 20:30:00	61	0	17.36	12.55	0
27-08-09 20:45:00	60	0	17.25	12.55	0
27-08-09 21:00:00	60	0	17.16	12.55	0
27-08-09 21:15:00	60	0	17.11	12.55	0
27-08-09 21:30:00	60	0	17.04	12.55	0
27-08-09 21:45:00	60	0	16.96	12.55	0
27-08-09 22:00:00	60	0	16.89	12.55	0
27-08-09 22:15:00	59	0	16.82	12.55	0
27-08-09 22:30:00	59	0	16.76	12.55	0
27-08-09 22:45:00	60	0	16.7	12.55	0
27-08-09 23:00:00	60	0	16.65	12.55	0
27-08-09 23:15:00	59	0	16.61	12.55	0
27-08-09 23:30:00	59	0	16.59	12.55	0
27-08-09 23:45:00	59	0	16.58	12.55	0

28-08-09 00:00:00	59	0	16.52	12.55	0
28-08-09 00:15:00	59	0	16.44	12.55	0
28-08-09 00:30:00	59	0	16.36	12.55	0
28-08-09 00:45:00	59	0	16.28	12.55	0
28-08-09 01:00:00	59	0	16.2	12.55	0
28-08-09 01:15:00	59	0	16.1	12.55	0
28-08-09 01:30:00	59	0	15.93	12.55	0
28-08-09 01:45:00	59	0	15.77	12.55	0
28-08-09 02:00:00	59	0	15.65	12.55	0
28-08-09 02:15:00	59	0	15.54	12.55	0
28-08-09 02:30:00	59	0	15.42	12.55	0
28-08-09 02:45:00	59	0	15.31	12.55	0
28-08-09 03:00:00	59	0	15.21	12.52	0
28-08-09 03:15:00	59	0	15.12	12.52	0
28-08-09 03:30:00	60	0	15.04	12.52	0
28-08-09 03:45:00	59	0	14.97	12.52	0
28-08-09 04:00:00	59	0	14.91	12.52	0
28-08-09 04:15:00	59	0	14.84	12.52	0
28-08-09 04:30:00	59	0	14.78	12.52	0
28-08-09 04:45:00	59	0	14.73	12.52	0
28-08-09 05:00:00	59	0	14.66	12.52	0
28-08-09 05:15:00	59	0	14.61	12.52	0
28-08-09 05:30:00	59	0	14.55	12.52	0
28-08-09 05:45:00	59	0	14.51	12.52	0
28-08-09 06:00:00	60	0	14.45	12.52	0
28-08-09 06:15:00	60	0	14.41	12.52	0
28-08-09 06:30:00	60	0	14.39	12.52	0
28-08-09 06:45:00	60	0	14.34	12.52	0
28-08-09 07:00:00	60	0	14.29	12.52	0
28-08-09 07:15:00	60	0	14.28	12.52	0
28-08-09 07:30:00	60	0	14.28	12.52	0
28-08-09 07:45:00	60	0	14.28	12.52	0
28-08-09 08:00:00	60	0	14.28	12.52	0
28-08-09 08:15:00	60	0	14.35	12.52	0
28-08-09 08:30:00	60	0	14.55	12.52	0
28-08-09 08:45:00	60	0	14.9	12.52	0
28-08-09 09:00:00	59	0	15.36	12.52	0
28-08-09 09:15:00	59	0	15.92	12.52	0
28-08-09 09:30:00	60	0	16.48	12.52	0
28-08-09 09:45:00	60	0	17.02	12.52	0
28-08-09 10:00:00	59	0	17.41	12.52	0
28-08-09 10:15:00	59	0	17.32	12.52	0
28-08-09 10:30:00	59	0	17.06	12.52	0
28-08-09 10:45:00	59	0	16.93	12.52	0
28-08-09 11:00:00	59	0	16.87	12.52	0
28-08-09 11:15:00	59	0	16.8	12.52	0
28-08-09 11:30:00	60	0	17.07	12.52	0
28-08-09 11:45:00	60	0	17.9	12.52	0
28-08-09 12:00:00	59	0	18.79	12.52	0
28-08-09 12:15:00	59	0	19.08	12.55	0
28-08-09 12:30:00	59	647	18.99	12.52	12.383
28-08-09 12:45:00	60	971	18.64	12.52	18.811
28-08-09 13:00:00	60	971	18.28	12.52	19.095
28-08-09 13:15:00	60	971	18.02	12.52	19.063

28-08-09 13:30:00	60	971	17.8	12.52	18.998
28-08-09 13:45:00	60	971	17.61	12.52	18.966
28-08-09 14:00:00	60	971	17.69	12.52	18.901
28-08-09 14:15:00	60	971	17.8	12.52	18.843
28-08-09 14:30:00	60	971	17.63	12.52	18.998
28-08-09 14:45:00	60	971	17.43	12.52	19.063
28-08-09 15:00:00	61	971	17.31	12.52	19.193
28-08-09 15:15:00	60	971	17.28	12.52	18.908
28-08-09 15:30:00	60	971	17.2	12.52	18.849
28-08-09 15:45:00	60	971	17.17	12.52	18.94
28-08-09 16:00:00	60	971	17.11	12.52	18.759
28-08-09 16:15:00	60	971	16.94	12.52	19.005
28-08-09 16:30:00	61	971	16.77	12.52	19.128
28-08-09 16:45:00	61	971	16.64	12.52	19.128
28-08-09 17:00:00	60	971	16.54	12.52	18.901
28-08-09 17:15:00	60	971	16.45	12.52	19.031
28-08-09 17:30:00	60	971	16.4	12.52	18.934
28-08-09 17:45:00	60	971	16.33	12.52	18.972
28-08-09 18:00:00	60	971	16.26	12.52	18.843
28-08-09 18:15:00	60	971	16.18	12.52	18.947
28-08-09 18:30:00	60	971	16.07	12.52	18.765
28-08-09 18:45:00	61	971	15.97	12.52	19.16
28-08-09 19:00:00	61	971	15.94	12.52	19.16
28-08-09 19:15:00	61	971	15.99	12.52	19.128
28-08-09 19:30:00	61	971	15.94	12.52	19.29
28-08-09 19:45:00	60	971	15.88	12.52	19.096
28-08-09 20:00:00	61	971	15.79	12.52	19.128
28-08-09 20:15:00	60	971	15.73	12.52	18.998
28-08-09 20:30:00	61	971	15.66	12.52	19.322
28-08-09 20:45:00	61	971	15.61	12.52	19.128
28-08-09 21:00:00	61	971	15.56	12.52	19.193
28-08-09 21:15:00	61	971	15.5	12.52	19.16
28-08-09 21:30:00	60	971	15.43	12.52	19.031
28-08-09 21:45:00	61	971	15.36	12.52	19.225
28-08-09 22:00:00	61	971	15.29	12.52	19.193
28-08-09 22:15:00	61	971	15.24	12.52	19.141
28-08-09 22:30:00	61	971	15.15	12.52	19.251
28-08-09 22:45:00	60	971	15.09	12.52	19.115
28-08-09 23:00:00	60	971	15.01	12.52	18.985
28-08-09 23:15:00	61	971	14.97	12.52	19.27
28-08-09 23:30:00	60	971	14.89	12.52	19.018
28-08-09 23:45:00	60	971	14.83	12.52	19.057
29-08-09 00:00:00	60	971	14.77	12.52	18.998
29-08-09 00:15:00	60	971	14.71	12.52	19.108
29-08-09 00:30:00	60	971	14.67	12.52	18.882
29-08-09 00:45:00	60	971	14.61	12.52	19.031
29-08-09 01:00:00	59	971	14.55	12.52	18.661
29-08-09 01:15:00	59	971	14.48	12.52	18.506
29-08-09 01:30:00	59	971	14.42	12.52	18.629
29-08-09 01:45:00	59	971	14.35	12.52	18.629
29-08-09 02:00:00	59	971	14.3	12.52	18.655
29-08-09 02:15:00	59	971	14.27	12.52	18.59
29-08-09 02:30:00	59	971	14.21	12.5	18.577
29-08-09 02:45:00	59	971	14.15	12.5	18.655

29-08-09 03:00:00	59	971	14.08	12.52	18.59
29-08-09 03:15:00	59	971	13.99	12.5	18.552
29-08-09 03:30:00	59	971	13.92	12.5	18.519
29-08-09 03:45:00	58	971	13.88	12.5	18.202
29-08-09 04:00:00	59	971	13.81	12.5	18.273
29-08-09 04:15:00	59	971	13.76	12.5	18.241
29-08-09 04:30:00	59	971	13.71	12.5	18.435
29-08-09 04:45:00	59	971	13.67	12.5	18.526
29-08-09 05:00:00	59	971	13.62	12.5	18.493
29-08-09 05:15:00	59	971	13.6	12.5	18.37
29-08-09 05:30:00	59	971	13.55	12.5	18.312
29-08-09 05:45:00	59	971	13.55	12.5	18.26
29-08-09 06:00:00	59	971	13.55	12.5	18.422
29-08-09 06:15:00	59	971	13.55	12.5	18.338
29-08-09 06:30:00	58	971	13.55	12.5	18.189
29-08-09 06:45:00	58	971	13.51	12.5	18.137
29-08-09 07:00:00	59	971	13.47	12.5	18.247
29-08-09 07:15:00	58	971	13.42	12.5	18.176
29-08-09 07:30:00	62	971	13.42	12.5	20.073
29-08-09 07:45:00	63	971	13.42	12.5	20.164
29-08-09 08:00:00	62	971	13.43	12.5	20.034
29-08-09 08:15:00	62	971	13.49	12.5	19.937
29-08-09 08:30:00	62	971	13.71	12.5	19.872
29-08-09 08:45:00	62	971	14.12	12.5	19.808
29-08-09 09:00:00	62	971	14.65	12.5	19.711
29-08-09 09:15:00	62	971	15.29	12.5	19.743
29-08-09 09:30:00	62	971	16.02	12.5	19.743
29-08-09 09:45:00	62	971	16.76	12.5	19.808
29-08-09 10:00:00	62	971	17.46	12.5	19.613
29-08-09 10:15:00	61	971	18.12	12.5	19.516
29-08-09 10:30:00	61	971	18.8	12.52	19.451
29-08-09 10:45:00	61	971	19.41	12.52	19.419
29-08-09 11:00:00	61	971	19.92	12.52	19.419
29-08-09 11:15:00	61	971	20.46	12.52	19.231
29-08-09 11:30:00	61	971	20.54	12.52	19.128
29-08-09 11:45:00	61	971	20.04	12.52	19.322
29-08-09 12:00:00	60	971	19.52	12.52	19.031
29-08-09 12:15:00	61	971	19.31	12.52	19.128
29-08-09 12:30:00	61	971	18.93	12.52	19.167
29-08-09 12:45:00	61	971	18.52	12.52	19.128
29-08-09 13:00:00	60	971	18.16	12.52	19.031
29-08-09 13:15:00	60	971	18	12.52	18.869
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29-08-09 14:00:00	60	1283	17.92	12.52	24.855
29-08-09 14:15:00	60	1283	17.91	12.52	24.804
29-08-09 14:30:00	60	1283	17.8	12.52	24.906
29-08-09 14:45:00	60	1283	17.72	12.52	24.735
29-08-09 15:00:00	60	1283	17.55	12.52	24.735
29-08-09 15:15:00	59	1283	17.43	12.52	24.573
29-08-09 15:30:00	59	1283	17.34	12.52	24.479
29-08-09 15:45:00	59	1283	17.23	12.52	24.359
29-08-09 16:00:00	59	1283	17.13	12.52	24.393
29-08-09 16:15:00	59	1283	16.98	12.52	24.325

29-08-09 16:30:00	59	1283	16.83	12.52	24.342
29-08-09 16:45:00	59	1283	16.69	12.52	24.325
29-08-09 17:00:00	59	1283	16.56	12.52	24.256
29-08-09 17:15:00	59	1283	16.48	12.52	24.291
29-08-09 17:30:00	59	1283	16.42	12.52	24.222
29-08-09 17:45:00	59	1283	16.31	12.52	24.102
29-08-09 18:00:00	59	1283	16.19	12.52	24.188
29-08-09 18:15:00	58	1283	16.06	12.52	24.034
29-08-09 18:30:00	58	1283	15.89	12.52	23.965
29-08-09 18:45:00	58	1283	15.73	12.52	23.846
29-08-09 19:00:00	58	1283	15.59	12.52	23.888
29-08-09 19:15:00	58	1283	15.47	12.52	23.88
29-08-09 19:30:00	58	1283	15.36	12.52	23.906
29-08-09 19:45:00	58	1283	15.23	12.52	23.683
29-08-09 20:00:00	58	1283	15.11	12.52	23.846
29-08-09 20:15:00	58	1283	15.04	12.52	23.692
29-08-09 20:30:00	58	1283	15	12.52	23.563
29-08-09 20:45:00	58	1283	14.96	12.52	23.965
29-08-09 21:00:00	58	1283	14.91	12.52	23.803
29-08-09 21:15:00	58	1283	14.87	12.52	23.829
29-08-09 21:30:00	58	1283	14.82	12.52	23.503
29-08-09 21:45:00	58	1283	14.8	12.52	23.632
29-08-09 22:00:00	58	1283	14.76	12.52	23.674
29-08-09 22:15:00	58	1283	14.74	12.52	23.658
29-08-09 22:30:00	58	1283	14.74	12.5	23.675
29-08-09 22:45:00	58	1283	14.74	12.52	23.623
29-08-09 23:00:00	58	1283	14.74	12.5	23.683
29-08-09 23:15:00	58	1283	14.74	12.5	23.623
29-08-09 23:30:00	58	1283	14.67	12.5	23.546
29-08-09 23:45:00	58	1283	14.67	12.5	23.658
30-08-09 00:00:00	58	1283	14.63	12.5	23.666
30-08-09 00:15:00	58	1283	14.6	12.5	23.709
30-08-09 00:30:00	58	1283	14.55	12.5	23.709
30-08-09 00:45:00	58	1283	14.54	12.5	23.555
30-08-09 01:00:00	58	1283	14.54	12.5	23.666
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30-08-09 05:15:00	57	1283	14.35	12.5	22.99
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30-08-09 05:45:00	57	1283	14.34	12.5	23.127

30-08-09 06:00:00	57	1283	14.35	12.5	22.965
30-08-09 06:15:00	57	1283	14.34	12.5	22.879
30-08-09 06:30:00	56	1283	14.34	12.5	22.7
30-08-09 06:45:00	56	1283	14.34	12.5	22.725
30-08-09 07:00:00	57	1283	14.33	12.5	22.896
30-08-09 07:15:00	56	1283	14.29	12.5	22.46
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30-08-09 07:45:00	56	1283	14.34	12.5	22.452
30-08-09 08:00:00	56	1283	14.34	12.5	22.554
30-08-09 08:15:00	55	1283	14.4	12.5	22.101
30-08-09 08:30:00	55	1283	14.52	12.5	21.896
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30-08-09 12:15:00	53	1414	17.95	12.52	23.001
30-08-09 12:30:00	53	1414	17.76	12.52	22.803
30-08-09 12:45:00	53	1414	17.67	12.52	23.029
30-08-09 13:00:00	53	1414	17.63	12.52	22.935
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30-08-09 15:30:00	52	1414	17.25	12.52	22.463
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30-08-09 16:15:00	52	1414	17.25	12.52	22.208
30-08-09 16:30:00	52	1414	17.19	12.52	22.293
30-08-09 16:45:00	52	1414	17.1	12.52	22.246
30-08-09 17:00:00	52	1414	17.01	12.52	22.067
30-08-09 17:15:00	52	1414	16.96	12.52	22.218
30-08-09 17:30:00	52	1414	16.91	12.52	22.058
30-08-09 17:45:00	52	1414	16.83	12.52	22.058
30-08-09 18:00:00	51	1414	16.76	12.52	21.963
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30-08-09 18:45:00	52	1414	16.64	12.52	22.171
30-08-09 19:00:00	52	1414	16.59	12.5	22.208
30-08-09 19:15:00	52	1414	16.58	12.5	22.076

30-08-09 19:30:00	52	1414	16.53	12.52	22.246
30-08-09 19:45:00	52	1414	16.5	12.5	22.171
30-08-09 20:00:00	52	1414	16.45	12.5	22.407
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30-08-09 20:45:00	53	1414	16.38	12.5	22.784
30-08-09 21:00:00	53	1414	16.36	12.5	22.784
30-08-09 21:15:00	53	1414	16.32	12.5	22.699
30-08-09 21:30:00	53	1414	16.32	12.5	23
30-08-09 21:45:00	53	1414	16.31	12.5	22.868
30-08-09 22:00:00	52	1414	16.28	12.5	22.586
30-08-09 22:15:00	53	1414	16.28	12.5	22.887
30-08-09 22:30:00	53	1414	16.32	12.5	22.925
30-08-09 22:45:00	54	1414	16.31	12.5	23.33
30-08-09 23:00:00	53	1414	16.32	12.5	23.095
30-08-09 23:15:00	53	1414	16.32	12.5	23.17
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31-08-09 00:00:00	53	1414	16.34	12.5	22.755
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31-08-09 01:00:00	53	1414	16.39	12.5	23.038
31-08-09 01:15:00	53	1414	16.39	12.5	23.113
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31-08-09 02:00:00	53	1414	16.41	12.5	22.963
31-08-09 02:15:00	53	1414	16.44	12.5	23.085
31-08-09 02:30:00	53	1414	16.45	12.5	23.095
31-08-09 02:45:00	53	1414	16.45	12.5	22.887
31-08-09 03:00:00	52	1414	16.45	12.5	22.623
31-08-09 03:15:00	53	1414	16.45	12.5	23.057
31-08-09 03:30:00	53	1414	16.45	12.5	22.755
31-08-09 03:45:00	53	1414	16.45	12.5	22.915
31-08-09 04:00:00	53	1414	16.44	12.5	22.991
31-08-09 04:15:00	53	1414	16.42	12.5	22.783
31-08-09 04:30:00	53	1414	16.43	12.5	22.718
31-08-09 04:45:00	53	1414	16.45	12.5	22.661
31-08-09 05:00:00	53	1414	16.43	12.5	23.123
31-08-09 05:15:00	53	1414	16.39	12.5	22.896
31-08-09 05:30:00	52	1414	16.39	12.5	22.633
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31-08-09 06:00:00	52	1414	16.39	12.5	22.501
31-08-09 06:15:00	53	1414	16.4	12.5	22.746
31-08-09 06:30:00	52	1414	16.42	12.5	22.208
31-08-09 06:45:00	52	1414	16.42	12.5	22.076
31-08-09 07:00:00	52	1414	16.45	12.5	22.322
31-08-09 07:15:00	51	1414	16.45	12.5	21.85
31-08-09 07:30:00	51	1414	16.47	12.5	21.85
31-08-09 07:45:00	51	1414	16.53	12.5	21.473
31-08-09 08:00:00	51	1414	16.6	12.5	21.944
31-08-09 08:15:00	51	1414	16.65	12.5	21.765
31-08-09 08:30:00	51	1414	16.72	12.5	21.473
31-08-09 08:45:00	51	1414	16.77	12.5	21.633

31-08-09 09:00:00	51	1414	16.85	12.5	21.445
31-08-09 09:15:00	50	1414	16.92	12.5	21.35
31-08-09 09:30:00	51	1414	16.97	12.5	21.511
31-08-09 09:45:00	50	1414	17.03	12.5	21.209
31-08-09 10:00:00	50	1414	17.14	12.5	20.935
31-08-09 10:15:00	50	1414	17.86	12.5	20.747
31-08-09 10:30:00	49	1242	19.18	12.5	17.886
31-08-09 10:45:00	49	1128	20.07	12.5	16.302
31-08-09 11:00:00	49	1128	20.99	12.5	16.197
31-08-09 11:15:00	49	1128	21.44	12.5	16.159
31-08-09 11:30:00	49	1128	21.08	12.5	16.37
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31-08-09 12:00:00	50	1128	20.16	12.5	16.904
31-08-09 12:15:00	50	1128	20.09	12.5	16.799
31-08-09 12:30:00	50	1128	20.4	12.52	16.648
31-08-09 12:45:00	50	1128	20.35	12.52	16.693
31-08-09 13:00:00	49	1128	20.16	12.52	16.31
31-08-09 13:15:00	49	1128	20.02	12.52	16.31
31-08-09 13:30:00	49	1128	19.85	12.52	16.295
31-08-09 13:45:00	49	1128	19.73	12.52	16.265
31-08-09 14:00:00	49	1128	19.57	12.52	16.302
31-08-09 14:15:00	49	1128	19.45	12.52	16.205
31-08-09 14:30:00	49	1128	19.4	12.52	16.174
31-08-09 14:45:00	48	1128	19.44	12.52	16.002
31-08-09 15:00:00	48	1128	19.49	12.52	16.002
31-08-09 15:15:00	48	1128	19.55	12.52	15.753
31-08-09 15:30:00	48	1128	19.61	12.52	15.904
31-08-09 15:45:00	48	1128	19.56	12.52	15.987
31-08-09 16:00:00	48	1128	19.49	12.52	15.776
31-08-09 16:15:00	48	1128	19.46	12.52	15.776
31-08-09 16:30:00	48	1128	19.37	12.52	15.784
31-08-09 16:45:00	49	1128	19.3	12.52	16.077
31-08-09 17:00:00	48	1165	19.19	12.52	16.389
31-08-09 17:15:00	48	1411	19.08	12.52	19.81
31-08-09 17:30:00	48	1505	19.03	12.52	21.197
31-08-09 17:45:00	48	1552	18.95	12.52	21.758
31-08-09 18:00:00	48	1552	18.83	12.52	21.924
31-08-09 18:15:00	48	1552	18.76	12.52	21.872
31-08-09 18:30:00	49	1552	18.71	12.52	22.286
31-08-09 18:45:00	48	1552	18.61	12.52	21.903
31-08-09 19:00:00	48	1552	18.47	12.5	21.81
31-08-09 19:15:00	48	1552	18.37	12.5	21.851
31-08-09 19:30:00	48	1552	18.27	12.52	21.934
31-08-09 19:45:00	48	1552	18.17	12.5	21.717
31-08-09 20:00:00	48	1552	18.04	12.5	21.52
31-08-09 20:15:00	48	1552	17.93	12.5	21.417
31-08-09 20:30:00	47	1552	17.81	12.5	21.313
31-08-09 20:45:00	47	1552	17.71	12.5	21.21
31-08-09 21:00:00	48	1552	17.6	12.5	21.417
31-08-09 21:15:00	47	1552	17.51	12.5	21.292
31-08-09 21:30:00	47	1552	17.41	12.5	21.044
31-08-09 21:45:00	48	1552	17.32	12.5	21.748
31-08-09 22:00:00	47	1552	17.24	12.5	20.961
31-08-09 22:15:00	47	1552	17.16	12.5	20.837

31-08-09 22:30:00	47	1552	17.09	12.5	20.92
31-08-09 22:45:00	46	1552	16.99	12.5	20.755
31-08-09 23:00:00	46	1552	16.85	12.5	20.465
31-08-09 23:15:00	46	1552	16.71	12.5	20.341
31-08-09 23:30:00	46	1552	16.61	12.5	20.465
31-08-09 23:45:00	46	1552	16.52	12.5	20.589
01-09-09 00:00:00	46	1552	16.45	12.5	20.682
01-09-09 00:15:00	47	1552	16.44	12.5	20.92
01-09-09 00:30:00	46	1552	16.41	12.5	20.424
01-09-09 00:45:00	47	1552	16.39	12.5	20.837
01-09-09 01:00:00	47	1552	16.38	12.5	20.92
01-09-09 01:15:00	46	1552	16.36	12.5	20.631
01-09-09 01:30:00	47	1552	16.33	12.5	21.013
01-09-09 01:45:00	46	1552	16.3	12.5	20.589
01-09-09 02:00:00	46	1552	16.23	12.5	20.672
01-09-09 02:15:00	46	1552	16.16	12.5	20.341
01-09-09 02:30:00	45	1552	16.08	12.5	20.093
01-09-09 02:45:00	45	1552	16.02	12.5	20.134
01-09-09 03:00:00	45	1552	15.99	12.5	19.844
01-09-09 03:15:00	46	1552	15.99	12.5	20.217
01-09-09 03:30:00	45	1552	15.97	12.5	19.834
01-09-09 03:45:00	45	1552	15.9	12.5	19.979
01-09-09 04:00:00	45	1552	15.79	12.47	19.875
01-09-09 04:15:00	45	1552	15.68	12.47	20.124
01-09-09 04:30:00	45	1552	15.61	12.47	19.73
01-09-09 04:45:00	45	1552	15.52	12.47	19.699
01-09-09 05:00:00	45	1552	15.46	12.47	19.544
01-09-09 05:15:00	44	1552	15.35	12.47	19.327
01-09-09 05:30:00	45	1552	15.21	12.47	19.555
01-09-09 05:45:00	44	1552	15.13	12.47	19.317
01-09-09 06:00:00	44	1552	15.13	12.47	19.255
01-09-09 06:15:00	44	1552	15.13	12.47	19.41
01-09-09 06:30:00	44	1552	15.12	12.47	19.079
01-09-09 06:45:00	44	1552	15.11	12.47	19.254
01-09-09 07:00:00	44	1552	15.09	12.47	18.985
01-09-09 07:15:00	44	1552	15.07	12.47	18.851
01-09-09 07:30:00	43	1552	15.09	12.47	18.737
01-09-09 07:45:00	43	1552	15.13	12.47	18.499
01-09-09 08:00:00	43	1552	15.2	12.47	18.406
01-09-09 08:15:00	43	1552	15.31	12.47	18.282
01-09-09 08:30:00	42	1552	15.67	12.47	17.868
01-09-09 08:45:00	42	1552	16.31	12.47	17.661
01-09-09 09:00:00	42	1552	17	12.47	17.537
01-09-09 09:15:00	42	1552	17.74	12.47	17.702
01-09-09 09:30:00	42	1552	18.46	12.47	17.537
01-09-09 09:45:00	42	1552	19	12.47	17.537
01-09-09 10:00:00	41	1552	19.45	12.47	17.412
01-09-09 10:15:00	42	1438	19.92	12.47	16.248
01-09-09 10:30:00	41	1362	20.37	12.47	15.135
01-09-09 10:45:00	41	1362	20.98	12.5	15.026
01-09-09 11:00:00	41	1362	20.98	12.5	14.917
01-09-09 11:15:00	41	1362	20.6	12.5	15.063
01-09-09 11:30:00	41	1362	20.19	12.5	15.026
01-09-09 11:45:00	41	1362	20.06	12.5	14.99

01-09-09 12:00:00	41	1362	19.76	12.5	15.026
01-09-09 12:15:00	41	1362	19.48	12.5	14.917
01-09-09 12:30:00	41	1362	19.53	12.5	14.881
01-09-09 12:45:00	41	1362	19.2	12.5	14.881
01-09-09 13:00:00	41	1362	18.83	12.5	14.845
01-09-09 13:15:00	40	1362	18.61	12.5	14.699
01-09-09 13:30:00	40	1362	18.38	12.5	14.699
01-09-09 13:45:00	40	1362	18.03	12.5	14.663
01-09-09 14:00:00	40	1362	17.81	12.5	14.591
01-09-09 14:15:00	40	1362	17.66	12.5	14.554
01-09-09 14:30:00	40	1362	17.55	12.5	14.591
01-09-09 14:45:00	40	1362	17.41	12.5	14.518
01-09-09 15:00:00	40	1362	17.32	12.5	14.554
01-09-09 15:15:00	40	1362	17.15	12.5	14.482
01-09-09 15:30:00	41	1362	16.84	12.5	15.172
01-09-09 15:45:00	43	1362	16.67	12.5	15.971
01-09-09 16:00:00	43	1362	16.65	12.5	16.007
01-09-09 16:15:00	43	1362	16.78	12.5	16.125
01-09-09 16:30:00	43	1362	16.91	12.5	16.116
01-09-09 16:45:00	43	1362	16.92	12.47	16.007
01-09-09 17:00:00	43	1362	16.87	12.5	16.044
01-09-09 17:15:00	43	1362	16.77	12.5	16.08
01-09-09 17:30:00	43	1362	16.72	12.47	16.125
01-09-09 17:45:00	43	1362	16.72	12.47	16.316
01-09-09 18:00:00	43	1362	16.72	12.47	16.28
01-09-09 18:15:00	43	1362	16.72	12.47	16.189
01-09-09 18:30:00	43	1362	16.68	12.47	16.352
01-09-09 18:45:00	43	1362	16.53	12.47	16.162
01-09-09 19:00:00	44	1362	16.39	12.47	16.534
01-09-09 19:15:00	43	1362	16.3	12.47	16.307
01-09-09 19:30:00	43	1362	16.15	12.47	16.153
01-09-09 19:45:00	43	1362	15.98	12.47	16.234
01-09-09 20:00:00	43	1362	15.9	12.47	16.416
01-09-09 20:15:00	43	1362	15.86	12.47	16.443
01-09-09 20:30:00	44	1362	15.85	12.47	16.57
01-09-09 20:45:00	44	1362	15.77	12.47	16.516
01-09-09 21:00:00	43	1362	15.65	12.47	16.343
01-09-09 21:15:00	44	1362	15.57	12.47	16.661
01-09-09 21:30:00	44	1362	15.48	12.47	16.616
01-09-09 21:45:00	44	1362	15.42	12.47	16.543
01-09-09 22:00:00	44	1362	15.33	12.47	16.579
01-09-09 22:15:00	43	1362	15.28	12.47	16.425
01-09-09 22:30:00	44	1362	15.22	12.47	16.543
01-09-09 22:45:00	44	1362	15.19	12.47	16.543
01-09-09 23:00:00	44	1362	15.13	12.47	16.743
01-09-09 23:15:00	43	1362	15.08	12.47	16.361
01-09-09 23:30:00	43	1362	15.03	12.47	16.461
01-09-09 23:45:00	43	1362	15	12.47	16.207
02-09-09 00:00:00	43	1362	14.95	12.47	16.153
02-09-09 00:15:00	42	1362	14.91	12.47	15.898
02-09-09 00:30:00	42	1362	14.86	12.47	15.717
02-09-09 00:45:00	42	1362	14.8	12.47	15.68
02-09-09 01:00:00	42	1362	14.78	12.47	15.717
02-09-09 01:15:00	42	1362	14.74	12.47	15.499

02-09-09 01:30:00	42	1362	14.7	12.47	15.499
02-09-09 01:45:00	42	1362	14.67	12.44	15.462
02-09-09 02:00:00	42	1362	14.66	12.47	15.462
02-09-09 02:15:00	42	1362	14.61	12.44	15.462
02-09-09 02:30:00	42	1362	14.61	12.44	15.462
02-09-09 02:45:00	41	1362	14.54	12.44	15.317
02-09-09 03:00:00	42	1362	14.48	12.44	15.426
02-09-09 03:15:00	41	1362	14.46	12.44	15.281
02-09-09 03:30:00	41	1362	14.45	12.44	15.281
02-09-09 03:45:00	41	1362	14.46	12.44	15.208
02-09-09 04:00:00	41	1362	14.47	12.44	15.172
02-09-09 04:15:00	41	1362	14.46	12.44	15.172
02-09-09 04:30:00	41	1362	14.41	12.44	15.208
02-09-09 04:45:00	41	1362	14.36	12.44	15.208
02-09-09 05:00:00	41	1362	14.34	12.44	15.026
02-09-09 05:15:00	41	1362	14.3	12.44	15.208
02-09-09 05:30:00	41	1362	14.28	12.44	14.954
02-09-09 05:45:00	41	1362	14.24	12.44	14.954
02-09-09 06:00:00	41	1362	14.21	12.44	14.954
02-09-09 06:15:00	41	1362	14.21	12.44	14.881
02-09-09 06:30:00	41	1362	14.21	12.44	14.845
02-09-09 06:45:00	41	1362	14.21	12.44	14.881
02-09-09 07:00:00	41	1362	14.21	12.44	14.881
02-09-09 07:15:00	41	1362	14.24	12.44	14.917
02-09-09 07:30:00	41	1362	14.28	12.44	14.845
02-09-09 07:45:00	41	1362	14.32	12.44	14.845
02-09-09 08:00:00	40	1362	14.36	12.44	14.772
02-09-09 08:15:00	40	1362	14.43	12.44	14.663
02-09-09 08:30:00	40	1362	14.53	12.44	14.591
02-09-09 08:45:00	40	1362	14.61	12.44	14.663
02-09-09 09:00:00	40	1362	14.68	12.44	14.591
02-09-09 09:15:00	40	1362	14.75	12.44	14.409
02-09-09 09:30:00	40	1362	14.99	12.44	14.409

Time	Depth	Velocity	Temperature	Battery	Flow Rate
13/11/09	(Av.) mm	(Av.) mm/s	(Av.) ºC	(RAW) V	(Av.) l/s
13-11-09 00:00:00	408	0	11.04	11.73	0
13-11-09 00:15:00	403	0	11.04	11.73	0
13-11-09 00:30:00	399	0	11.05	11.73	0
13-11-09 00:45:00	395	0	11.14	11.73	0
13-11-09 01:00:00	392	0	11.24	11.73	0
13-11-09 01:15:00	389	0	11.09	11.73	0
13-11-09 01:30:00	387	0	11.04	11.73	0
13-11-09 01:45:00	384	0	11.04	11.73	0
13-11-09 02:00:00	382	0	11.09	11.73	0
13-11-09 02:15:00	380	0	11.11	11.73	0
13-11-09 02:30:00	379	0	11.11	11.73	0
13-11-09 02:45:00	377	0	11.05	11.73	0
13-11-09 03:00:00	376	0	10.99	11.73	0
13-11-09 03:15:00	375	0	10.99	11.73	0
13-11-09 03:30:00	374	0	10.98	11.73	0
13-11-09 03:45:00	372	0	10.98	11.73	0
13-11-09 04:00:00	371	0	10.92	11.73	0
13-11-09 04:15:00	370	0	10.95	11.7	0
13-11-09 04:30:00	369	0	11.12	11.73	0
13-11-09 04:45:00	368	0	10.92	11.7	0
13-11-09 05:00:00	367	0	10.94	11.7	0
13-11-09 05:15:00	366	0	11.05	11.7	0
13-11-09 05:30:00	365	0	10.96	11.7	0
13-11-09 05:45:00	363	0	10.73	11.7	0
13-11-09 06:00:00	362	0	10.76	11.7	0
13-11-09 06:15:00	361	0	10.79	11.7	0
13-11-09 06:30:00	360	0	10.7	11.7	0
13-11-09 06:45:00	359	0	10.65	11.7	0
13-11-09 07:00:00	358	0	10.65	11.7	0
13-11-09 07:15:00	357	0	10.66	11.7	0
13-11-09 07:30:00	356	0	10.69	11.7	0
13-11-09 07:45:00	355	0	10.62	11.7	0
13-11-09 08:00:00	354	0	10.6	11.7	0
13-11-09 08:15:00	353	0	10.58	11.7	0
13-11-09 08:30:00	352	0	10.73	11.7	0
13-11-09 08:45:00	351	135	10.78	11.7	33.331
13-11-09 09:00:00	350	0	10.65	11.7	0
13-11-09 09:15:00	349	5	10.65	11.7	1.306
13-11-09 09:30:00	348	166	10.66	11.7	40.65
13-11-09 09:45:00	347	0	10.72	11.7	0
13-11-09 10:00:00	346	0	10.67	11.7	0
13-11-09 10:15:00	345	0	10.68	11.7	0
13-11-09 10:45:00	344	0	11.19	13.05	0
13-11-09 11:00:00	344	0	11.2	13	0
13-11-09 11:15:00	343	2	11.12	13	0.699
13-11-09 11:30:00	341	0	10.91	13	0
13-11-09 11:45:00	340	0	10.84	13	0
13-11-09 12:00:00	339	0	10.84	13	0

13-11-09 12:15:00	338	0	10.83	12.97	0
13-11-09 12:30:00	337	0	10.94	12.97	0
13-11-09 12:45:00	336	190	10.91	12.97	44.333
13-11-09 13:00:00	335	0	10.84	12.97	0
13-11-09 13:15:00	334	0	10.84	12.97	0
13-11-09 13:30:00	333	0	10.84	12.97	0
13-11-09 13:45:00	332	0	10.84	12.95	0
13-11-09 14:00:00	331	4	10.9	12.95	0.911
13-11-09 14:15:00	330	0	11.07	12.95	0
13-11-09 14:30:00	329	0	10.95	12.95	0
13-11-09 14:45:00	328	0	10.91	12.95	0
13-11-09 15:00:00	327	0	10.91	12.95	0
13-11-09 15:15:00	327	0	10.92	12.95	0
13-11-09 15:30:00	326	1	10.96	12.95	0.385
13-11-09 15:45:00	325	353	11.15	12.95	78.163
13-11-09 16:00:00	324	4	10.98	12.95	0.928
13-11-09 16:15:00	323	0	10.93	12.95	0
13-11-09 16:30:00	322	0	10.96	12.95	0
13-11-09 16:45:00	321	0	10.91	12.95	0
13-11-09 17:00:00	320	5	10.91	12.92	1.218
13-11-09 17:15:00	320	0	10.91	12.92	0
13-11-09 17:30:00	319	0	10.91	12.92	0
13-11-09 17:45:00	318	0	10.91	12.92	0
13-11-09 18:00:00	320	5	10.99	12.92	1.165
13-11-09 18:15:00	327	0	11.01	12.92	0
13-11-09 18:30:00	343	7	11	12.92	1.863
13-11-09 18:45:00	365	1	10.99	12.92	0.437
13-11-09 19:00:00	383	4	10.98	12.92	1.237
13-11-09 19:15:00	395	1	11	12.92	0.505
13-11-09 19:30:00	399	0	11.04	12.92	0
13-11-09 19:45:00	402	4	11.04	12.92	1.33
13-11-09 20:00:00	414	12	11.05	12.92	3.966
13-11-09 20:15:00	422	24	11.03	12.92	7.869
13-11-09 20:30:00	421	20	11.01	12.92	6.559
13-11-09 20:45:00	416	25	11.04	12.92	7.884
13-11-09 21:00:00	412	12	11.04	12.92	3.738
13-11-09 21:15:00	407	3	11.04	12.92	1.087
13-11-09 21:30:00	403	7	11.1	12.92	2.144
13-11-09 21:45:00	400	8	11.1	12.92	2.35
13-11-09 22:00:00	397	5	11.04	12.92	1.552
13-11-09 22:15:00	394	6	11.06	12.92	1.769
13-11-09 22:30:00	391	0	11.1	12.92	0
13-11-09 22:45:00	389	0	11.11	12.92	0
13-11-09 23:00:00	387	0	11.16	12.92	0
13-11-09 23:15:00	385	3	11.17	12.92	0.966
13-11-09 23:30:00	383	6	11.11	12.92	1.697
13-11-09 23:45:00	382	8	11.13	12.92	2.39

Time **21/11/09**	Depth (Av.) mm	Velocity (Av.) mm/s	Temperature (Av.) ºC	Battery (RAW) V	Flow Rate (Av.) l/s
21-11-09 00:00:00	263	0	10.32	12.55	0
21-11-09 00:15:00	262	0	10.31	12.55	0
21-11-09 00:30:00	262	0	10.28	12.55	0
21-11-09 00:45:00	261	0	10.25	12.52	0
21-11-09 01:00:00	261	0	10.24	12.52	0
21-11-09 01:15:00	260	0	10.18	12.52	0
21-11-09 01:30:00	259	0	10.18	12.52	0
21-11-09 01:45:00	259	0	10.18	12.52	0
21-11-09 02:00:00	258	0	10.18	12.52	0
21-11-09 02:15:00	258	0	10.18	12.52	0
21-11-09 02:30:00	258	0	10.18	12.52	0
21-11-09 02:45:00	257	0	10.17	12.52	0
21-11-09 03:00:00	257	0	10.39	12.52	0
21-11-09 03:15:00	256	0	10.51	12.52	0
21-11-09 03:30:00	256	0	10.51	12.52	0
21-11-09 03:45:00	255	0	10.6	12.52	0
21-11-09 04:00:00	255	0	10.59	12.52	0
21-11-09 04:15:00	255	0	10.58	12.52	0
21-11-09 04:30:00	254	0	10.58	12.52	0
21-11-09 04:45:00	254	0	10.55	12.52	0
21-11-09 05:00:00	253	0	10.57	12.55	0
21-11-09 05:15:00	253	0	10.63	12.55	0
21-11-09 05:30:00	252	0	10.61	12.55	0
21-11-09 05:45:00	252	0	10.6	12.55	0
21-11-09 06:00:00	251	8	10.63	12.55	1.345
21-11-09 06:15:00	251	0	10.65	12.55	0
21-11-09 06:30:00	251	0	10.65	12.55	0
21-11-09 06:45:00	250	0	10.68	12.55	0
21-11-09 07:00:00	250	0	10.66	12.55	0
21-11-09 07:15:00	249	0	10.65	12.55	0
21-11-09 07:30:00	249	0	10.71	12.55	0
21-11-09 07:45:00	249	0	10.71	12.55	0
21-11-09 08:00:00	248	0	10.71	12.55	0
21-11-09 08:15:00	248	0	10.73	12.55	0
21-11-09 08:30:00	247	0	10.78	12.55	0
21-11-09 08:45:00	247	0	10.78	12.55	0
21-11-09 09:00:00	247	0	10.78	12.55	0
21-11-09 09:15:00	246	0	10.8	12.55	0
21-11-09 09:30:00	246	0	10.84	12.55	0
21-11-09 09:45:00	246	0	10.82	12.55	0
21-11-09 10:00:00	245	0	10.87	12.55	0
21-11-09 10:15:00	245	0	10.84	12.55	0
21-11-09 10:30:00	244	0	10.84	12.55	0
21-11-09 10:45:00	244	0	10.9	12.55	0
21-11-09 11:00:00	243	0	10.91	12.55	0
21-11-09 11:15:00	243	0	10.92	12.55	0
21-11-09 11:30:00	243	0	10.96	12.55	0
21-11-09 11:45:00	243	0	10.91	12.55	0

21-11-09 12:00:00	242	0	10.91	12.55	0
21-11-09 12:15:00	242	0	10.99	12.55	0
21-11-09 12:30:00	242	0	10.99	12.55	0
21-11-09 12:45:00	241	0	10.99	12.55	0
21-11-09 13:00:00	241	0	11.03	12.55	0
21-11-09 13:15:00	241	0	11.04	12.55	0
21-11-09 13:30:00	240	0	11.06	12.55	0
21-11-09 13:45:00	240	0	11.14	12.55	0
21-11-09 14:00:00	240	0	11.17	12.55	0
21-11-09 14:15:00	239	0	11.15	12.55	0
21-11-09 14:30:00	239	0	11.17	12.55	0
21-11-09 14:45:00	239	0	11.22	12.55	0
21-11-09 15:00:00	239	1	11.25	12.55	0.24
21-11-09 15:15:00	239	4	11.24	12.55	0.643
21-11-09 15:30:00	239	5	11.24	12.55	0.787
21-11-09 15:45:00	239	0	11.27	12.55	0
21-11-09 16:00:00	239	3	11.31	12.55	0.536
21-11-09 16:15:00	238	2	11.26	12.55	0.336
21-11-09 16:30:00	238	8	11.29	12.55	1.17
21-11-09 16:45:00	238	0	11.31	12.55	0
21-11-09 17:00:00	238	5	11.32	12.55	0.768
21-11-09 17:15:00	238	5	11.32	12.55	0.778
21-11-09 17:30:00	239	8	11.51	12.52	1.203
21-11-09 17:45:00	240	1	11.66	12.52	0.26
21-11-09 18:00:00	248	6	11.7	12.52	1.022
21-11-09 18:15:00	264	8	11.75	12.52	1.485
21-11-09 18:30:00	287	17	11.77	12.52	3.191
21-11-09 18:45:00	316	14	11.8	12.52	3.108
21-11-09 19:00:00	342	26	11.84	12.52	6.288
21-11-09 19:15:00	357	0	11.83	12.52	0
21-11-09 19:30:00	363	17	11.83	12.52	4.616
21-11-09 19:45:00	364	5	11.81	12.52	1.537
21-11-09 20:00:00	365	0	11.79	12.52	0
21-11-09 20:15:00	365	0	11.78	12.52	0
21-11-09 20:30:00	365	0	11.77	12.52	0
21-11-09 20:45:00	364	0	11.77	12.52	0
21-11-09 21:00:00	363	1	11.77	12.52	0.484
21-11-09 21:15:00	362	0	11.76	12.52	0
21-11-09 21:30:00	361	0	11.77	12.52	0
21-11-09 21:45:00	360	0	11.77	12.52	0
21-11-09 22:00:00	360	0	11.77	12.52	0
21-11-09 22:15:00	359	0	11.77	12.52	0
21-11-09 22:30:00	358	0	11.77	12.52	0
21-11-09 22:45:00	357	0	11.79	12.52	0
21-11-09 23:00:00	356	0	11.78	12.52	0
21-11-09 23:15:00	355	0	11.8	12.5	0
21-11-09 23:30:00	354	0	11.77	12.5	0
21-11-09 23:45:00	354	0	11.77	12.5	0

Time	Depth	Velocity	Temperature	Battery	Flow Rate
07/12/09	**(Av.) mm**	**(Av.) mm/s**	**(Av.) ºC**	**(RAW) V**	**(Av.) l/s**
07-12-09 00:00:00	387	0	9.48	11.65	0
07-12-09 00:15:00	387	0	9.39	11.65	0
07-12-09 00:30:00	387	0	9.39	11.65	0
07-12-09 00:45:00	386	0	9.39	11.65	0
07-12-09 01:00:00	387	0	9.39	11.65	0
07-12-09 01:15:00	387	0	9.39	11.65	0
07-12-09 01:30:00	386	0	9.39	11.65	0
07-12-09 01:45:00	386	0	9.45	11.65	0
07-12-09 02:00:00	386	0	9.43	11.65	0
07-12-09 02:15:00	386	5	9.41	11.65	1.454
07-12-09 02:30:00	386	4	9.43	11.65	1.118
07-12-09 02:45:00	386	2	9.42	11.65	0.801
07-12-09 03:00:00	386	0	9.45	11.65	0
07-12-09 03:15:00	386	0	9.46	11.65	0
07-12-09 03:30:00	386	0	9.46	11.65	0
07-12-09 03:45:00	386	0	9.46	11.65	0
07-12-09 04:00:00	386	0	9.46	11.65	0
07-12-09 04:15:00	385	141	9.46	11.65	39.586
07-12-09 04:30:00	385	0	9.46	11.65	0
07-12-09 04:45:00	385	0	9.46	11.65	0
07-12-09 05:00:00	385	0	9.5	11.65	0
07-12-09 05:15:00	385	79	9.52	11.65	22.073
07-12-09 05:30:00	385	0	9.53	11.65	0
07-12-09 05:45:00	385	0	9.52	11.62	0
07-12-09 06:00:00	385	0	9.52	11.62	0
07-12-09 06:15:00	385	0	9.52	11.62	0
07-12-09 06:30:00	385	0	9.52	11.62	0
07-12-09 06:45:00	385	0	9.52	11.62	0
07-12-09 07:00:00	385	0	9.52	11.62	0
07-12-09 07:15:00	385	0	9.52	11.62	0
07-12-09 07:30:00	385	0	9.52	11.62	0
07-12-09 07:45:00	385	0	9.52	11.62	0
07-12-09 08:00:00	385	3	9.5	11.62	1.077
07-12-09 08:15:00	385	0	9.51	11.62	0
07-12-09 08:30:00	385	0	9.49	11.62	0
07-12-09 08:45:00	385	43	9.5	11.62	12.151
07-12-09 09:00:00	385	0	9.49	11.62	0
07-12-09 09:15:00	385	0	9.48	11.62	0
07-12-09 09:30:00	385	0	9.59	11.62	0
07-12-09 09:45:00	385	0	9.55	11.62	0
07-12-09 10:00:00	384	0	9.53	11.62	0
07-12-09 10:15:00	385	0	9.57	11.62	0
07-12-09 10:30:00	385	0	9.59	11.62	0
07-12-09 10:45:00	385	0	9.6	11.62	0
07-12-09 11:00:00	385	314	9.66	11.62	87.697
07-12-09 11:15:00	385	0	9.62	11.62	0
07-12-09 11:30:00	385	0	9.68	11.62	0
07-12-09 11:45:00	384	0	9.64	11.62	0

07-12-09 12:00:00	384	0	9.63	11.62	0
07-12-09 12:15:00	385	132	9.58	11.62	36.825
07-12-09 12:30:00	384	0	9.59	11.62	0
07-12-09 12:45:00	384	0	9.59	11.62	0
07-12-09 13:00:00	384	4	9.52	11.62	1.17
07-12-09 13:30:00	385	0	9.56	12.97	0
07-12-09 13:45:00	385	0	9.28	12.95	0
07-12-09 14:00:00	384	0	9.22	12.92	0
07-12-09 14:15:00	385	1	9.22	12.89	0.464
07-12-09 14:30:00	385	3	9.14	12.89	1.077
07-12-09 14:45:00	384	2	9.05	12.87	0.631
07-12-09 15:00:00	385	4	9.05	12.87	1.323
07-12-09 15:15:00	388	2	9.06	12.84	0.636
07-12-09 15:30:00	400	31	9.04	12.84	9.335
07-12-09 15:45:00	409	39	9	12.84	12.044
07-12-09 16:00:00	414	6	9.06	12.81	2.072
07-12-09 16:15:00	417	19	9.13	12.81	5.957
07-12-09 16:30:00	419	33	9.08	12.81	10.464
07-12-09 16:45:00	419	14	9.07	12.81	4.379
07-12-09 17:00:00	416	2	9.17	12.81	0.659
07-12-09 17:15:00	413	0	9.18	12.81	0
07-12-09 17:30:00	410	3	9.18	12.81	0.915
07-12-09 17:45:00	407	0	9.19	12.79	0
07-12-09 18:00:00	405	0	9.25	12.79	0
07-12-09 18:15:00	403	0	9.22	12.79	0
07-12-09 18:30:00	401	0	9.31	12.79	0
07-12-09 18:45:00	399	5	9.42	12.79	1.617
07-12-09 19:00:00	398	1	9.29	12.79	0.446
07-12-09 19:15:00	396	0	9.26	12.79	0
07-12-09 19:30:00	395	3	9.26	12.79	0.926
07-12-09 19:45:00	394	0	9.3	12.79	0
07-12-09 20:00:00	393	0	9.41	12.79	0
07-12-09 20:15:00	392	0	9.34	12.79	0
07-12-09 20:30:00	392	0	9.36	12.79	0
07-12-09 20:45:00	391	0	9.41	12.76	0
07-12-09 21:00:00	390	0	9.35	12.79	0
07-12-09 21:15:00	390	0	9.33	12.79	0
07-12-09 21:30:00	389	2	9.33	12.76	0.586
07-12-09 21:45:00	389	0	9.33	12.76	0
07-12-09 22:00:00	389	179	9.51	12.76	50.811
07-12-09 22:15:00	388	0	9.41	12.76	0
07-12-09 22:30:00	388	0	9.47	12.76	0
07-12-09 22:45:00	388	7	9.41	12.76	1.989
07-12-09 23:00:00	387	0	9.38	12.76	0
07-12-09 23:15:00	387	0	9.33	12.76	0
07-12-09 23:30:00	387	0	9.33	12.76	0
07-12-09 23:45:00	387	0	9.33	12.76	0

Appendix 4

Raw data and calculation of EMC for storm 1 and storm 2

Storm 1 (21/11/2009)

TSS

Time	Q, l/s	TSS, mg/l	Δt, s	Q_{av}, l/s	C, mg/l	QCΔt	QΔt
16.45	0	119.5					
				0.384	59.75	20650	345
17.00	0.768	119.5	900				
				0.773	119.5	83136	695
17.15	0.778	119.5	900				
				0.991	67.25	59980	892
17.30	1.203	15	900				
				0.732	10.5	6917	658
17.45	0.26	6	900				
				0.641	11.5	6635	577
18.00	1.022	17	900				
				1.254	30	33858	1129
18.15	1.485	43	900				
				2.338	40	84168	2104
18.30	3.191	37	900				
				3.150	36	102060	2835
18.45	3.108	35	900				
				1.554	35	48951	1398
19.00	0	35	900				
						Σ 446354	Σ 10633

EMC TSS = 41.98 mg/l

TOC

Time	Q, l/s	TOC, mg/l	Δt, s	Q_{av}, l/s	C, mg/l	QCΔt	QΔt
16.45	0	7.78					
				0.384	7.78	2689	345
17.00	0.768	7.78	900				
				0.773	7.78	5413	695
17.15	0.778	7.78	900				
				0.991	8.05	7180	892
17.30	1.203	8.31	900				
				0.732	7.36	4849	658
17.45	0.26	6.4	900				
				0.641	6.13	3536	577
18.00	1.022	5.85	900				
				1.254	6.29	7099	1129
18.15	1.485	6.72	900				
				2.338	7.03	14792	2104
18.30	3.191	7.33	900				
				3.150	7.99	22652	2835
18.45	3.108	8.66	900				
				1.554	8.66	12111	1398
19.00	0	8.66	900				
						Σ 80322	Σ 10637

EMC TOC = 7.55 mg/l

Zntot

Time	Q, l/s	Zntot, mg/l	Δt, s	Q_{av}, l/s	C, mg/l	QCΔt	QΔt
16.45	0	0.273					
				0.384	0.273	94.348	345
17.00	0.768	0.273	900				
				0.773	0.273	189.926	695
17.15	0.778	0.273	900				
				0.991	0.176	156.974	892
17.30	1.203	0.079	900				
				0.732	0.095	62.586	658
17.45	0.26	0.111	900				
				0.641	0.096	55.382	577
18.00	1.022	0.081	900				
				1.254	0.093	104.96	1129
18.15	1.485	0.105	900				
				2.338	0.105	220.941	2104
18.30	3.191	0.105	900				
				3.150	0.098	277.83	2835
18.45	3.108	0.091	900				
				1.554	0.091	127.27	1398
19.00	0	0.091	900				
						Σ1290.3	Σ10635.3

EMC Zntot = 0.121 mg/l

Zndis

Time	Q, l/s	Zndis, mg/l	Δt, s	Q_{av}, l/s	C, mg/l	QCΔt	QΔt
16.45	0	0.025					
				0.384	0.025	8.64	345
17.00	0.768	0.025	900				
				0.773	0.025	17.393	695
17.15	0.778	0.025	900				
				0.991	0.025	22.298	892
17.30	1.203	0.025	900				
				0.732	0.0245	16.141	658
17.45	0.26	0.024	900				
				0.641	0.026	14.999	577
18.00	1.022	0.028	900				
				1.254	0.0265	29.908	1129
18.15	1.485	0.025	900				
				2.338	0.0255	53.657	2104
18.30	3.191	0.026	900				
				3.150	0.0265	75.128	2835
18.45	3.108	0.027	900				
				1.554	0.027	37.762	1398
19.00	0	0.027	900				
						Σ 275.9	Σ 10635.3

EMC Zndis = 0.026 mg/l

Fetot

Time	Q, l/s	Fetot, mg/l	Δt, s	Q_{av}, l/s	C, mg/l	QCΔt	QΔt
16.45	0	3.76					
				0.384	3.76	1299.5	345
17.00	0.768	3.76	900				
				0.773	3.76	2615.8	695
17.15	0.778	3.76	900				
				0.991	2.376	2119.2	892
17.30	1.203	0.659	900				
				0.732	1.027	676.6	658
17.45	0.26	1.395	900				
				0.641	1.089	628.2	577
18.00	1.022	0.782	900				
				1.254	1.077	1215.5	1129
18.15	1.485	1.371	900				
				2.338	1.311	2758.6	2104
18.30	3.191	1.251	900				
				3.150	1.179	3342.4	2835
18.45	3.108	1.106	900				
				1.554	1.106	1546.8	1398
19.00	0	1.106	900				
						Σ 16202.6	Σ 10635.3

EMC Fetot = 1.523 mg/l

Fedis

Time	Q, l/s	Fedis, mg/l	Δt, s	Q_{av}, l/s	C, mg/l	QCΔt	QΔt
16.45	0	0.94					
				0.384	0.94	324.8	345
17.00	0.768	0.94	900				
				0.773	0.94	653.9	695
17.15	0.778	0.94	900				
				0.991	0.506	451.3	892
17.30	1.203	0.073	900				
				0.732	0.072	47.4	658
17.45	0.26	0.07	900				
				0.641	0.071	40.9	577
18.00	1.022	0.072	900				
				1.254	0.069	77.8	1129
18.15	1.485	0.066	900				
				2.338	0.072	151.5	2104
18.30	3.191	0.077	900				
				3.150	0.075	212.6	2835
18.45	3.108	0.073	900				
				1.554	0.073	102.1	1398
19.00	0	0.073	900				
						Σ 2062.6	Σ 10635.5

EMC Fedis = 0.194 mg/l

Na

Time	Q, l/s	Na, mg/l	Δt, s	Q_{av}, l/s	C, mg/l	QCΔt	QΔt
16.45	0	57.25					
				0.384	57.25	19786	345
17.00	0.768	57.25	900				
				0.773	57.25	39829	695
17.15	0.778	57.25	900				
				0.991	56.39	50294	892
17.30	1.203	55.54	900				
				0.732	56.71	37361	658
17.45	0.26	57.88	900				
				0.641	56.65	32681	577
18.00	1.022	55.41	900				
				1.254	55.87	63055	1129
18.15	1.485	56.34	900				
				2.338	55.80	117414	2104
18.30	3.191	55.26	900				
				3.150	57.87	164062	2835
18.45	3.108	60.49	900				
				1.554	60.49	84601	1398
19.00	0	60.49	900				
						Σ 609083	Σ 10633

EMC Na = 57.28 mg/l

Storm 2 (07/12/2009)

TSS

Time	Q, l/s	TSS, mg/l	Δt, s	Qav,l/s	C, mg/l	QCΔt	QΔt
14.00	0	14					
				0.232	12.5	2610	308
14.15	0.464	11	900				
				0.771	11.25	7806	693
14.30	1.077	11.5	900				
				0.854	12.0	9223	768
14.45	0.631	12.5	900				
				0.977	11.0	9672	879
15.00	1.323	9.5	900				
				0.980	9.25	8159	882
15.15	0.636	9	900				
				4.986	9.25	41508	4487
15.30	9.335	9.5	900				
				10.689	9.25	88986	9620
15.45	12.044	9	900				
				6.022	9.0	48778	5420
16.00	0	9	900				
						Σ 216742	Σ 22959

EMC TSS = 9.44 mg/l

TOC

Time	Q, l/s	TOC, mg/l	Δt, s	Qav,l/s	C, mg/l	QCΔt	QΔt
14.00	0	3.32					
				0.232	3.65	762.12	308
14.15	0.464	3.98	900				
				0.771	5.775	4007.3	693
14.30	1.077	7.57	900				
				0.854	8.94	6871.3	768
14.45	0.631	10.31	900				
				0.977	6.55	5759.4	879
15.00	1.323	2.79	900				
				0.980	3.15	2778.3	882
15.15	0.636	3.51	900				
				4.986	4.52	20283	4487
15.30	9.335	5.53	900				
				10.689	5.69	54690	9620
15.45	12.044	5.84	900				
				6.022	5.84	31652	5420
16.00	0	5.84	900				
						Σ 126803	Σ 22959

EMC TOC = 5.52 mg/l

Zntot

Time	Q, l/s	Zntot, mg/l	Δt, s	Qav,l/s	C, mg/l	QCΔt	QΔt
14.00	0	0.081					
				0.232	0.075	15.66	308
14.15	0.464	0.068	900				
				0.771	0.071	49.27	693
14.30	1.077	0.073	900				
				0.854	0.079	60.72	768
14.45	0.631	0.084	900				
				0.977	0.082	72.10	879
15.00	1.323	0.08	900				
				0.980	0.086	75.85	882
15.15	0.636	0.092	900				
				4.986	0.097	435.28	4487
15.30	9.335	0.102	900				
				10.689	0.096	923.53	9620
15.45	12.044	0.09	900				
				6.022	0.09	487.78	5420
16.00	0	0.09	900				
						Σ 2120.2	Σ 22959

EMC Zntot = 0.092 mg/l

Zndis

Time	Q, l/s	Zndis, mg/l	Δt, s	Qav,l/s	C, mg/l	QCΔt	QΔt
14.00	0	0.04					
				0.232	0.039	8.143	308
14.15	0.464	0.038	900				
				0.771	0.038	26.368	693
14.30	1.077	0.039	900				
				0.854	0.042	32.281	768
14.45	0.631	0.044	900				
				0.977	0.044	38.689	879
15.00	1.323	0.044	900				
				0.980	0.045	39.69	882
15.15	0.636	0.046	900				
				4.986	0.048	215.39	4487
15.30	9.335	0.049	900				
				10.689	0.053	509.86	9620
15.45	12.044	0.056	900				
				6.022	0.056	303.508	5420
16.00	0	0.056	900				
						Σ 1173.9	Σ 22959

EMC Zndis = 0.052 mg/l

Fetot

Time	Q, l/s	Fetot, mg/l	Δt, s	Qav,l/s	C, mg/l	QCΔt	QΔt
14.00	0	0.726					
				0.232	0.723	150.96	308
14.15	0.464	0.719	900				
				0.771	0.716	496.8	693
14.30	1.077	0.712	900				
				0.854	0.72	553.4	768
14.45	0.631	0.728	900				
				0.977	0.695	611.1	879
15.00	1.323	0.661	900				
				0.980	0.677	597.1	882
15.15	0.636	0.692	900				
				4.986	0.662	2970.6	4487
15.30	9.335	0.632	900				
				10.689	0.667	6406.9	9620
15.45	12.044	0.7	900				
				6.022	0.7	3793.9	5420
16.00	0	0.7	900				
						Σ 15580.7	Σ 22959

EMC Fetot = 0.679 mg/l

Fedis

Time	Q, l/s	Fedis, mg/l	Δt, s	Qav,l/s	C, mg/l	QCΔt	QΔt
14.00	0	0.143					
				0.232	0.12	25.06	308
14.15	0.464	0.096	900				
				0.771	0.091	63.145	693
14.30	1.077	0.086	900				
				0.854	0.083	63.794	768
14.45	0.631	0.08	900				
				0.977	0.08	70.344	879
15.00	1.323	0.079	900				
				0.980	0.082	72.324	882
15.15	0.636	0.084	900				
				4.986	0.077	345.53	4487
15.30	9.335	0.069	900				
				10.689	0.069	663.79	9620
15.45	12.044	0.068	900				
				6.022	0.068	368.55	5420
16.00	0	0.068	900				
						Σ 1672.5	Σ 22959

EMC Fedis = 0.073 mg/l

Appendix 5

Raw data of metals taken from the M1 and Woodbrook

M1 (WET AND DRY WEATHER)

date N of sample	**wet** Fe$_{tot}$ mg/l	**wet** Fe$_{dis}$ mg/
11/07/2008		
inl_1.20 pm	1.471	0.177
inl_1.40 pm	2.677	0.155
inl_2.00 pm	2.273	0.185
inl_2.30 pm	2.705	0.147
inl_2.50 pm	1.551	0.15
a/w_2.50 pm	1.177	0.212
a/w_3.00 pm	1.133	0.196
09/09/2008		
inl_9.30 am	0.774	0.045
inl_9.45 am	2.478	0.04
inl_10.20 am	4.312	0.045
b/w_9.30 am	0.498	0.039
b/w_9.45 am	1.287	0.048
b/w_10.00 am	3.003	0.041
b/w_10.20 am	3.692	0.04
a/w_9.30 am	0.369	0.065
a/w_9.45 am	0.459	0.047
a/w_10.00 am	0.856	0.043
a/w_10.20 am	1.628	0.057
a/w_10.45 am	2.647	0.226
a/w_11.15 am	2.991	0.059
a/w_11.35 am	3.278	0.053
22/01/2009		
inl	7.09	0.147
b/w	1.405	0.397
ch	n/a	0.035
Flow (ch – a/w)	3.153	0.007
Flow (ch – a/w)	3.123	0.007
Flow (ch – a/w)	3.209	0.006
a/w	1.212	0.018
3	0.174	0.026
03/07/2009		
ch_8.45 am	0.934	0.177
inl_11.30 am	6.162	0.101
b/w_12.15 pm	0.962	0.171
b/w_2 pm	3.347	0.092
b/w_2.15 pm	5.248	0.063
b/w_2.30 pm	5.185	0.08
a/w_2 pm	0.597	0.171
a/w_2.15 pm	2.204	0.14
a/w_2.30 pm	1.617	0.152
13/11/2009_after rain		
inl_10.45 am	2.109	0.141
Inl_ 3.45 pm	1.597	0.092
ch_10.45 am	2.844	0.103
ch_3.45pm	2.128	0.099

date N of sample	**dry** Fe$_{tot}$ mg/l	**dry** Fe$_{dis}$ mg/l
17/12/07_3	0.735	0.04
17/12/07_b/w	1.525	0.037
03/01/08_3	0.228	0.022
03/01/08_b/w	2.734	0.026
03/01/08_a/w	1.123	0.031
14/04/08_3	0.277	0.029
14/04/08_b/w	0.658	0.123
14/04/08_a/w	0.388	0.029
14/04/08_inl	4.957	0.139
30/05/08_inl	0.847	0.118
30/05/08_b/w	0.943	0.077
30/05/08_a/w	0.68	0.078
30/05/08_3	0.526	0.066
26/06/08_b/w	0.397	0.19
26/06/08_a/w	0.22	0.091
26/06/08_3	0.526	0.066
29/07/08_ch_upper	0.234	0.091
29/07/08_ch_low	0.831	0.12
27/11/08_inl	1.724	0.056
27/11/08_b/w	0.518	0.083
27/11/08_ch_upper	0.389	0.059
27/11/08_ch_sediment	130	n/a
27/11/08_a/w	0.191	0.04
27/11/08_3	0.177	0.055
15/12/08_inl	0.899	0.018
15/12/08_b/w	0.878	0.022
15/12/08_ch	1.017	0.014
15/12/08_a/w	0.194	0.041
15/12/08_3	0.21	0.041
13/01/09_in	3.696	0.028
13/01/09_b/w	3.55	0.016
13/01/09_ch	0.309	0.02
13/01/09_a/w	0.291	0.033
13/01/09_3	0.277	0.034
03/03/09_inl	0.603	0.014
03/03/09_b/w	0.8	0.008
03/03/09_ch	0.112	0.004
03/03/09_a/w	0.159	0.025
03/03/09_3	0.177	0.025
21/04/09_inl	6.02	0.065
21/04/09_ch	0.632	0.03
21/04/09_a/w	0.767	0.057
21/04/09_3	0.241	0.054
14/05/09_3	0.822	0.037
14/05/09_b/w	2	0.044
14/05/09_ch	0.501	0.032
17/07/09_inl	1.519	0.067
17/07/09_b/w	0.524	0.148
17/07/09_ch	0.635	0.127
17/07/09_3	0.214	0.15

3_3.45pm	3.378	0.17
21/11/2009		
inl_5.15 pm	3.76	0.94
inl_5.30pm	0.659	0.073
inl_5.45pm	1.395	0.07
inl_6.00pm	0.782	0.072
inl_6.15pm	1.371	0.066
inl_6.30pm	1.251	0.077
inl_6.45pm	1.106	0.073
ch_5.15pm	1.285	0.086
ch_6.45pm	0.636	0.082
3_6.45pm	0.473	0.227
07/12/2009		
inl_2.00pm	0.726	0.143
inl_2.15pm	0.719	0.096
inl_2.30pm	0.712	0.086
Inl_2.45pm	0.728	0.08
inl_3 00pm	0.661	0.079
inl_3.15pm	0.692	0.084
inl_3.30pm	0.632	0.069
inl_3.45pm	0.7	0.068
a/w 2.00pm	1.021	0.079
a/w 3.00pm	1.158	0.101
a/w 3.45pm	1.283	0.079

18/08/09_ch	0.307	0.079
18/08/09_a/w	0.339	0.131
18/08/09_3	0.147	0.088
28/08/09_3	0.358	0.089
02/09/09_ch	0.665	0.274
02/09/09_3	0.674	0.102
03/09/09_ch	1.14	0.187
03/09/09_a/w	3.392	0.146
07/09/09_ch	0.428	0.158
07/09/09_a/w	7.386	0.091
09/09/09_ch	0.271	0.151
09/09/09_3	1.06	0.058
14/09/09_ch	0.796	0.094
14/09/09_3	1.211	0.111
16/09/09_ch	0.945	0.125
16/09/09_3	0.844	0.142
25/09/09_ch	0.574	0.012
25/09/09_3	4.076	0.091
29/09/09_ch	0.707	0.001
29/09/09_3	8.02	0.321
21/10/09_inl	1.904	0.008
21/10/09_ch	0.834	0.215
21/10/09_3	3.08	0.083
22/10/09_inl	2.562	0.028
22/10/09_ch	0.865	0.181
22/10/09_3	0.82	0.31
29/10/09_ch	1.154	0.079
29/10/09_3	4.87	0.024
05/11/09_inl	5.89	0.046
05/11/09_ch	0.821	0.124
05/11/09_3	2.243	0.15
09/11/09_inl	1.25	0.037
09/11/09_ch	0.713	0.122
09/11/09_3	2.066	0.101
10/11/09_inl	1.439	0.038
10/11/09_ch	0.564	0.114
10/11/09_3	2.849	0.122
24/11/09_inl	1.229	0.086
24/11/09_ch	0.897	0.11
24/11/09_3	0.419	0.214
02/12/09_inl	0.758	0.081
02/12/09_ch	0.819	0.074
02/12/09_3	0.706	0.192
09/12/09_inl	0.597	0.024
09/12/09_ch	0.892	0.036
09/12/09_3	0.447	0.169

date N of sample	**wet** Zn_{tot} mg/l	**wet** Zn_{dis} mg/l
11/07/2008		
inl_1.20 pm	0.152	0.047
inl_1.40 pm	0.169	0.027
inl_2.00 pm	0.168	0.024
inl_2.30 pm	0.177	0.023
inl_2.50 pm	0.147	0.026
a/w_2.50 pm	0.19	0.036
a/w_3.00 pm	0.123	0.032
09/09/2008		
inl_9.30 am	0.127	0.041
inl_9.45 am	0.131	0.046
inl_10.20 am	0.187	0.035
b/w_9.30 am	0.108	0.041
b/w_9.4 am	0.161	0.044
b/w_10.00 am	0.157	0.047
b/w_10.20 am	0.221	0.04
a/w_9.30 am	0.096	0.034
a/w_9.45 am	0.13	0.039
a/w_10.00 am	0.104	0.042
a/w_10.20 am	0.141	0.047
a/w_10.45 am	0.192	0.054
a/w_11.15 am	0.199	0.047
a/w_11.35 am	0.261	0.043
22/01/2009		
inl	0.312	0.048
b/w	0.177	0.033
ch	5.5	0.012
Flow (ch – a/w)	0.205	0.051
Flow (ch – a/w)	0.216	0.051
Flow (ch – a/w)	0.236	0.049
a/w	0.123	0.02
3	0.052	0
03/07/2009		
ch_8.45 am	0.044	0.007
inl_11.30 am	0.308	0.074
b/w_12.15 pm	0.046	0.019
b/w_2pm	0.165	0.044
b/w_2.15 pm	0.218	0.039
b/w_2.30 pm	0.203	0.038
a/w_2pm	0.031	0.005
a/w_2.15 pm	0.097	0.027
a/w_2.30 pm	0.079	0.025
13/11/2009_after rain		
inl_10.45 am	0.118	0.018
inl_3.45pm	0.098	0.058
ch_10.45 am	0.143	0.016
ch_3.45pm	0.12	0.012

date N of sample	**dry** Zn_{tot} mg/l	**dry** Zn_{dis} mg/l
17/12/07_3	0.093	0.07
17/12/07_b/w	0.057	0.011
03/01/08_3	0.014	0.007
03/01/08_b/w	0.152	0.048
03/01/08_a/w	0.07	0.016
14/04/08_3	0.041	0.011
14/04/08_b/w	0.13	0.025
14/04/08_a/w	0.054	0.009
14/04/08_inl	0.315	0.06
30/05/08_inl	0.228	0.137
30/05/08_b/w	0.156	0.097
30/05/08_a/w	0.134	0.098
30/05/08_3	0.08	0.069
26/06/08_b/w	0.11	0.02
26/06/08_a/w	0.081	0.012
26/06/08_3	0.051	0.017
29/07/08_ch_upper	0.05	0.014
29/07/08_ch_low	0.094	0.011
27/11/08_inl	0.165	0.069
27/11/08_b/w	0.075	0.029
27/11/08_ch_upper	0.127	0.099
27/11/08_ch_sediment	9.685	0.007
27/11/08_a/w	0.047	0.008
27/11/08_3	0.033	0.005
15/12/08_inl	0.076	0.038
15/12/08_b/w	0.094	0.077
15/12/08_ch	0.094	0.046
15/12/08_a/w	0.037	0.011
15/12/08_3	0.036	0.01
13/01/09_in	0.206	0.038
13/01/09_b/w	0.225	0.057
13/01/09_ch	0.155	0.152
13/01/09_a/w	0.04	0.012
13/01/09_3	0.047	0.008
03/03/09_inl	0.165	0.04
03/03/09_b/w	0.166	0.028
03/03/09_ch	0.135	0.026
03/03/09_a/w	0.091	0.004
03/03/09_3	0.024	0.003
21/04/09_inl	0.438	0.015
21/04/09_ch	0.176	0.013
21/04/09_a/w	0.188	0.011
21/04/09_3	0.153	0.01
14/05/09_3	0.099	0.018
14/05/09_b/w	0.255	0.009
14/05/09_ch	0.127	0.013
17/07/09_inl	0.164	0.022
17/07/09_b/w	0.043	0.009
17/07/09_ch	0.056	0.019
17/07/09_3	0.009	0

3_3.45pm	0.108	0.014
21/11/2009		
inl_5.15pm	0.273	0.025
inl_5.30pm	0.079	0.025
inl_5.45pm	0.111	0.024
inl_6.00pm	0.081	0.028
inl_6.15pm	0.105	0.025
inl_6.30pm	0.105	0.026
inl_6.45pm	0.091	0.027
ch_5.15pm	0.078	0.035
ch_6.45pm	0.074	0.034
3_6.45pm	0.04	0.007
07/12/2009		
inl_2.00pm	0.081	0.04
inl_2.15pm	0.068	0.038
inl_2.30pm	0.073	0.039
Inl_2.45pm	0.084	0.044
inl_3 00pm	0.08	0.044
inl_3.15pm	0.092	0.046
inl_3.30pm	0.102	0.049
inl_3.45pm	0.09	0.056
a/w 2.00pm	0.058	0.021
a/w 3.00pm	0.071	0.017
a/w 3.45pm	0.073	0.019

18/08/09_ch	0.019	0
18/08/09_a/w	0.007	0
18/08/09_3	0	0
28/08/09_3	0	0
02/09/09_ch	0	0
02/09/09_3	0	0
03/09/09_ch	0.009	0.008
03/09/09_a/w	0.14	0
07/09/09_ch	0	0
07/09/09_a/w	0.215	0
09/09/09_ch	0.033	0
09/09/09_3	0.044	0
14/09/09_ch	0.051	0.003
14/09/09_3	0.035	0
16/09/09_ch	0.047	0.003
16/09/09_3	0.012	0
25/09/09_ch	0.03	0
25/09/09_3	0.039	0
29/09/09_ch	0.064	0
29/09/09_3	0.094	0
21/10/09_inl	0.101	0.01
21/10/09_ch	0.066	0.024
21/10/09_3	0.051	0.01
22/10/09_inl	0.124	0.01
22/10/09_ch	0.069	0.023
22/10/09_3	0.023	0.014
29/10/09_ch	0.052	0.007
29/10/09_3	0.05	0.003
05/11/09_inl	0.264	0.019
05/11/09_ch	0.066	0.026
05/11/09_3	0.045	0.008
09/11/09_inl	0.087	0.01
09/11/09_ch	0.084	0.036
09/11/09_3	0.049	0.002
10/11/09_inl	0.095	0.005
10/11/09_ch	0.073	0.031
10/11/09_3	0.059	0
24/11/09_inl	0.092	0.032
24/11/09_ch	0.092	0.04
24/11/09_3	0.048	0.014
02/12/09_inl	0.086	0.032
02/12/09_ch	0.061	0.033
02/12/09_3	0.022	0.001
09/12/09_inl	0.103	0.086
09/12/09_ch	0.097	0.073
09/12/09_3	0.024	0.01

date N of sample	wet Cu_{tot} mg/l	wet Cu_{dis} mg/l
11/07/2008		
inl_1.20 pm	0.0137	0.0127
inl_1.40 pm	0.034	0.005
inl_2.00 pm	0.031	0.009
inl_2.30 pm	0.034	0.008
inl_2.50 pm	0.025	0.0109
a/w_2.50 pm	0	0
a/w_3.00 pm	0	0
09/09/2008		
inl_9.30 am	0.066	0.016
inl_9.45 am	0.086	0.019
inl_10.20 am	0.095	0.017
b/w_9.30 am	0.047	0.015
b/w_9.45 am	0.063	0.017
b/w_10.00 am	0.084	0.018
b/w_10.20 am	0.135	0.017
a/w_9.30 am	0.048	0.012
a/w_9.45 am	0.055	0.012
a/w_10.00 am	0.037	0.014
a/w_10.20 am	0.078	0.016
a/w_10.45 am	0.095	0.021
a/w_11.15 am	0.082	0.017
a/w_11.35 am	0.098	0.018
22/01/2009		
inl	0.167	0.008
b/w	0.253	0.002
ch	1.434	0
Flow (ch – a/w)	0.134	0.007
Flow (ch – a/w)	0.164	0.007
Flow (ch – a/w)	0.22	0.005
a/w	0.161	0
3	0.077	0
03/07/2009		
ch_8.45 am	0.014	0
inlet_11.30 am	0.135	0.042
b/w_12.15 am	0.022	0.005
b/w_2pm	0.085	0.024
b/w_2.15 pm	0.11	0.028
b/w_2.30 pm	0.094	0.029
a/w_2pm	0.004	0
a/w_2.15 pm	0.033	0.009
a/w_2.30 pm	0.024	0.006
13/11/2009_after rain		
inl_10.45 am	0.008	0
inl_3.45pm	0.003	0
ch_10.45 am	0.023	0
ch_3.45pm	0.007	0
3_3.45pm	0	0

date N of sample	dry Cu_{tot} mg/l	dry Cu_{dis} mg/l
17/12/07_3	0.013	0.009
17/12/07_b/w	0.008	0.005
03/01/08_3	0.005	0.003
03/01/08_b/w	0.033	0.016
03/01/08_a/w	0.025	0.007
14/04/08_3	0.003	0.003
14/04/08_b/w	0.012	0.002
14/04/08_a/w	0.016	0
14/04/08_inl	0.076	0.013
30/05/08_inl	0.047	0.029
30/05/08_b/w	0.044	0.02
30/05/08_a/w	0.035	0.016
30/05/08_3	0.041	0.009
26/06/08_b/w	0.025	0.002
26/06/08_a/w	0.025	0.003
26/06/08_3	0.029	0.006
29/07/08_ch_upper	0.014	0.003
29/07/08_ch_low	0.024	0.002
27/11/08_inl	0.035	0.008
27/11/08_b/w	0.008	0
27/11/08_ch_upper	0.003	0
27/11/8b/w'l	2.09	0
27/11/08_a/w	0.002	0
27/11/08_3	0.003	0.003
15/12/8_inl	0.025	0.007
15/12/8_b/w	0.023	0.007
15/12/8b/w'	0.026	0.006
15/12/8_a/w	0.011	0
15/12/8_3	0.013	0.003
13/01/9_in	0.042	0.007
13/01/9_b/w	0.042	0.007
13/01/9_b/w'	0	0
13/01/9_a/w	0.002	0
13/01/9_3	0.006	0
3/3/9_inl	0.03	0.01
3/3/9_b/w	0.023	0.004
3/3/9_upper	0.007	0.002
3/3/9_a/w	0.029	0
3/3/9_3M1	0.01	0
21/4/9_inl	0.096	0.028
21/4/9_b/w'	0.009	0.007
21/4/9_a/w	0	0
21/4/9_3M1	0	0
14/5/9_3M1	0.004	0
14/5/9_b/w	0.034	0.002
14/5/9_b/w'	0.003	0.002
17/7_inlet	0.049	0.014
17/7_b/w	0.012	0
17/7_chamber	0.011	0.003
17/7_3M1	0.006	0
18/8_chamber	0	0
18/8_a/w	0.003	0

21/11/2009		
inl_5.15pm	0.033	0.003
inl_5.30pm	0	0
inl_5.45pm	0	0
inl_6.00pm	0	0
inl_6.15pm	0	0
inl_6.30pm	0	0
inl_6.45pm	0	0
ch_5.15pm	0	0
ch_6.45pm	0	0
3_6.45pm	0	0
07/12/2009		
inl_2.00pm	0	0
inl_2.15pm	0	0
inl_2.30pm	0	0
Inl_2.45pm	0	0
inl_3 00pm	0	0
inl_3.15pm	0	0
inl_3.30pm	0	0
inl_3.45pm	0	0
a/w 2.00pm	0	0
a/w 3.00pm	0	0
a/w 3.45pm	0.002	0
18/8_3M1	0	0
28/8_3M1	0	0
2/9_Chamber	0	0
2/9_3M1	0	0
3/9_chamber	0	0
3/9_a/w	0.006	0
7/9_chamber	0	0
7/9_a/w	0.013	0
9/9_chamber	0	0
9/9_3M1	0	0
14/9_chamber	0	0
14/9_3M1	0	0
16/9_chamber	0	0
16/9_3M1	0	0
25/9_chamber	0	0
25/9_3M1	0	0
29/9_chamber	0	0
29/9_3M1	0.004	0
21/10/Inlet	0.022	0.004
21/10_chamber	0	0
21/10_3M1	0	0
22/10/Inlet	0.02	0.005
22/10_chamber	0	0
22/10_3M1	0	0
29/10_chamber	0	0
29/10_3M1	0	0
05/11_Inlet	0.042	0
05/11_chamber	0	0
05/11_3M1	0	0
09/11/09_Inlet	0	0
09/11/09_chamber	0	0
09/11/09_3M1	0	0
10/11/09_Inlet	0	0
10/11/09_chamber	0	0
10/11/09_3M1	0	0
24/11/09_inl	0	0
24/11/09_ch	0	0
24/11/09_3m1	0	0
02/12/09_inl	0	0
02/12/09_ch	0	0
02/12/09-3m1	0	0
09/12/09_inl	0	0
09/12/09_ch	0	0
09/12/09_3M1	0	0

inl – inlet (sample point N 1, see Fig. 4.2); b/w – before weir (sample point N 2, see Fig. 4.2); a/w - after weir (sample point N 3, see Fig. 4.2); 3M1 (3m1) – sample point N 4 (see Fig. 4.2); ch – chamber (see Photo 4.3 and Fig. 4.3); n/a – not analysed.

WOODBROOK (WET AND DRY WEATHER)

date N of sample	**wet** Fe_{tot}	**wet** Fe_{dis}	date N of sample	**dry** Fe_{tot}	**dry** Fe_{dis}
28/10/7_1	6.199	0.204	5/10/7_1	0.134	0.005
28/10/7_1	0.868	0.022	5/10/7_2	0.618	0.023
28/10/7_2	0.402	0.026	20/10/7_1	0.079	0.04
15/01/08_2	9.334	0.418	20/10/7_2	0.072	0.016
16/01/08_2	4.487	0.637	21/12/7_2	0.311	0.104
17/01/08_2	2.211	0.238	22/01/08_2	1.907	0.696
17/05/08_2	0.178	0.028	23/01/08_2	0.715	0.232
27/05/08_2	0.569	0.032	30/04/08_2	0.362	0.182
28/05/08_2	3.7	0.171	30/05/08_2	0.256	0.075
13/12/08_2	10.96	0.832	23/06/08_2	0.125	0.021
12/01/2009	0.832	0.08	23/07/08_2	0.321	0.011
22/01/2009	2.515	0.263	08/09/2008	0.528	0.222
15/04/2009	0.292	0.089	28/09/2008	0.143	0.063
07/07/09_morning	0.122	0.03	24/11/2008	0.277	0.04
07/07/09_afternoon	5.02	0.104	25/11/2008	0.165	0.028
29/07/2009	2.27	0.039	08/01/2009	0.479	0.025
			10/01/2009	0.132	0.048
			27/02/2009	0.16	0.092
			03/03/2009	0.168	0.016
			01/04/2009	0.064	0.017
			21/04/2009	0.261	0.005
			12/05/2009	0.099	0.006
			20/07/2009	0.168	0.063
			10/08_2009	0.114	0.042
			13/08/2009	0.121	0.014
			19/08/2009	0.071	0
			16/09/2009	0	0
			18/09/2009	0.025	0

date N of sample	wet W/d; Zn; tot	wet W/d; Zn; dis	date N of sample	dry W/d; Zn; tot	dry W/d; Zn; dis
28/10/2007	0.105	0.047	5/10/2007	0.026	0.012
28/10/2007	0.033	0.032	5/10/2007	0.028	0.018
28/10/2007	0.019	0.018	20/10/2007	0.016	0.011
15/01/2008	0.07	0.018	20/10/2007	0.02	0.017
16/01/2008	0.044	0.016	21/12/2007	0.011	0.004
17/01/2008	0.056	0.014	22/01/2008	0.022	0.015
17/05/2008	0.074	0.051	23/01/2008	0.056	0.016
27/05/2008	0.094	0.056	30/04/2008	0.039	0.019
28/05/2008	0.068	0.066	30/05/2008	0.05	0.014
13/12/2008	0.097	0.039	23/06/2008	0.044	0.019
12/01/2009	0.064	0.011	23/07/2008	0.055	0
22/01/2009	0.053	0.003	08/09/2008	0.079	0.003
15/04/2009	0.202	0.017	28/09/2008	0.028	0.004
07/07/09_morning	0.012	0.0043	24/11/2008	0.038	0.003
07/07/09_afternoon	0.081	0.003	25/11/2008	0.037	0.002
29/07/2009	0.051	0.002	08/01/2009	0.051	0.017
			10/01/2009	0.027	0
			27/02/2009	0	0
			03/03/2009	0	0
			01/04/2009	0.073	0
			21/04/2009	0.109	0.02
			12/05/2009	0.065	0.004

			20/07/2009	0.011	0.005
			10/08/2009	0.029	0
			13/08/2009	0	0
			19/08/2009	0	0
			16/09/2009	0	0
			18/09/2009	0.003	0

date N of sample	wet W/d; Cu; tot	wet W/d; Cu; dis	date N of sample	dry W/d; Cu; tot	dry W/d; Cu; dis
28/10/2007	0.04	0.021	21/12/2007	0.006	0.003
28/10/2007	0.01	0.009	22/01/2008	0.003	0.002
28/10/2007	0.005	0.004	23/01/2008	0.006	0.005
15/01/2008	0.013	0.004	30/04/2008	0.017	0
16/01/2008	0.01	0.008	30/05/2008	0.018	0.003
17/01/2008	0.011	0.003	23/06/2008	0.019	0.007
17/05/2008	0.025	0.003	23/07/2008	0	0
27/05/2008	0.027	0.002	08/09/2008	0.022	0.003
28/05/2008	0.039	0.003	28/09/2008	0.009	0.003
13/12/2008	0.022	0.006	24/11/2008	0.013	0.012
12/01/2009	0.011	0	25/11/2008	0.018	0
22/01/2009	0.103	0.003	08/01/2009	0	0
15/04/2009	0	0	10/01/2009	0.006	0.004
07/07/09_morning	0.011	0.003	27/02/2009	0.018	0
07/07/09_afternoon	0.027	0	03/03/2009	0.015	0
29/07/2009	0.003	0	01/04/2009	0	0
			21/04/2009	0.005	0.005
			12/05/2009	0.003	0.003
			20/07/2009	0	0
			10/08/2009	0	0
			13/08/2009	0	0
			19/08/2009	0	0
			16/09/2009	0	0
			18/09/2009	0	0

Appendix 6

Raw data for measured water quality parameters

RAINWATER SAMPLES TAKEN FROM 04.10.2006 TO 27.10.2006

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg/l	TSS, mg/l	NO_3^- mg/l
06.10.06	Woodbrook	Drizzle	7.8	360	590	2.4	3.95	3.0	17.23
09.10.06	M1 (J24)	Dry; T_{water}=14.5ºC; T_{sample}=17.9 ºC	7.3	180	210	5.9	5.01	6.0	2.27
09.10.06	M1(J24)	Dry; T_{water}=16.5ºC; T_{sample}=18.4 ºC	7.6	300	420	9.4	6.52	3.0	0.8
09.10.06	M1(J24)	Dry; T_{water}=15.0ºC; T_{sample}=18.2 ºC	7.3	270	380	73.5	6.38	72.0	0.68
11.10.06	Woodbrook	Heavy rain from10.00 am; cloudy; T_{sample}=18.4 ºC	7.2	140	370	36.5	4.4	250.0	5.62
12.10.06	Woodbrook	Dry; T_{water}=15.6ºC; T_{sample}=15.7 ºC	7.9	310	850	19.8	10.84	11.0	29.04
13.10.06	Woodbrook	Dry; foggy T_{water}=15.5ºC; T_{sample}=15.5 ºC	8.0	350	970	4.37	5.58	5.0	25.67
18.10.06	Woodbrook	Dry; cloudy; T_{sample}=16.9 ºC	7.8	410	1090	1.36	0.62	5.0	18.76
3M1 19.10.06	M1(J24)	Rain (drizzle); T_{water}=15.9ºC; Water depth = 23 cm.	6.8	210	560	22.0	8.94	19.0	0.33
3M1 19.10.06	M1 (J24) duplicate		6.8	230	610	19.6	7.68	15.4	2.29
20.10.06	Woodbrook	Heavy rain during night; water depth = 20 cm; T_{water}=13.8ºC; T_{air}=16.0ºC.	7.5	130	350	11.5	4.84	16.0	5.66
20.10.06	Woodbrook duplicate		7.4	120	330	11.0	5.95	12.5	5.26
3M1 26.10.06	M1 (J24)	Drizzle; water depth = 39 cm; T_{water}=13.7ºC; T_{air}=14.0ºC.	7.2	200	550	15.5	5.23	6.5	0.69
27.10.06	Woodbrook	Dry; water depth = 13.5 cm; T_{water}=10.8ºC; T_{air}=13.0ºC.	7.9	310	830	6.84	6.67	3.0	Not analysed

RAINWATER SAMPLES TAKEN FROM 07.11.2006 TO 27.11.2006

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg/l	TSS, mg/l	NO_3^-, mg/l
07.11.06	Woodbrook	Dry weather during two weeks; T_{air}= 9ºC; T_{water}=7.9ºC; depth of water = 10 cm	7.9	380	570	1.43	3.12	3.0	29.79
3M1 08.11.06	M1 (J24)	Rain (drizzle); T_{water}=7.7ºC; T_{air}= 12ºC; Depth of water = 11 cm	7.0	230	370	18.0	4.93	19.0	1.193
11.11.06	Woodbrook	Dry; windy; cloudy. T_{air}= 10ºC; Depth of water = 13 cm	7.6	310	540	1.87	5.94	3.0	21.50
* 11.11.06	Woodbrook	* - samples were collected immediately after rain at 9 pm.	7.2	230	370	23.3	Not analysed	36.0	14.05
17.11.06	Woodbrook	Drizzling during the whole night; water depth = 30 cm; T_{water}=7.9ºC; T_{air}=10.0ºC.	7.3	260	420	25.2	3.87	34.0	13.32
23.11.06	Woodbrook	Samples collection after rain; water depth = 19 cm; T_{water}=8.2ºC; T_{air}=10.0ºC.	7.2	190	310	131	17.72	126	31.82
3M1 23.11.06	M1 (J24)	T_{water}=7.7ºC; T_{air}= 10ºC;	7.0	240	390	15.2	6.08	17.0	2.35
27.11.06	Woodbrook	Dry; windy; cloudy. T_{air}= 10ºC; T_{water}=9.6ºC;	7.5	270	440	9.5	7.92	2.0	Not analysed

RAINWATER SAMPLES TAKEN FROM 06.12.2006 TO 19.12.2006

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg/l	TSS, mg/l	NO_3^- mg/l
06.12.06	Woodbrook	Drizzle during night; cumulus; T_{air}= 8ºC.	7.5	210	440	38.7	6.52	33.0	27.76
06.12.06	M1(24)	Drizzle during night; cumulus; T_{air}= 8ºC.	7.0	200	490	12.8	4.10	14.0	1.29
08.12.06	Woodbrook	Rain during night; T_{air}= 9ºC.	7.2	220	450	26.0	-	26.0	30.06
08.12.06	M1(24)	Rain during night; T_{air}= 9ºC.	7.1	190	380	15.0	3.85	10.0	4.21
11.12.06	Woodbrook	Heavy rain; T_{air}= 10ºC.	7.2	120	240	134	7.91	378.0	16.60
12.12.06	M1(24)	Rain started at 1.00 pm; samples were collected at 4.00 pm. T_{air}= 10ºC.	7.2	210	400	15.8	3.55	16.0	1.56
19.12.06	M1(24) junction	Dry	6.9	240	480	7.28	4.01	4.0	Not analysed

RAINWATER SAMPLES TAKEN FROM 11.01.2007 TO 23.02.2007

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg/l	TSS, mg/l	NO_3^- mg/l
13.02.07	Woodbrook	08.02.2007 – it was snowing; 09.02.2007 – it was thawing; T_{air}= 8ºC.	7.1	220	460	20.3	6.13	64.0	33.48
16.02.07	Woodbrook	Drizzle during night; T_{air}= 10ºC.	7.3	290	600	8.5	Not analysed	12.0	30.84
20.02.07	M1 (J24)	Dry	6.8	700	1440	12.8	3.06	13.0	1.03
Outlet of the lagoon 22.02.07	M1 (J24)	T_{air}= 10ºC;	7.2	670	1270	35.9	3.80	58.0	1.7
23.02.07	Woodbrook	Samples were collected at 4.00 pm during rain	7.3	170	360	68.8	8.82	51.0	24.01

RAINWATER SAMPLES TAKEN FROM 09.03.2007 TO 29.03.2007

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg/l	TSS, mg/l	NO_3^- mg/l
3M1 09.03.07	M1 (J24)	Dry, sunny. T_{air}= 10ºC; T_{water}= 8.7ºC; Depth of water = 74 cm	7.0	710	1380	3.97	3.29	8.0	1.375
3M1 29.03.07	M1(J24)	Drizzling T_{water}= 9.9ºC Sample was taken from a shallow place	7.6	710	1320	71.2	5.86	448.0	0.653

RAINWATER SAMPLES TAKEN FROM 11.04.2007 TO 30.04.2007

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg/l	TSS, mg/l	NO_3^- mg/l
3M1 11.04.07	M1 (J24)	Samples were taken from places with different water depth	7.5	750	1290	2.74	8.82	17.0	0.433
						32.4		200.0	
Final effluent	Loughborough sewage works		7.3	920	980	2.18	5.2	3.0	85.84
3M1 23.04.07	M1(J24)	Drizzling	7.4	820	1460	18.3	12.81	48.0	0.967
24.04.07	Woodbrook	Dry	8.1	270	520	2.71	4.78	5.0	18.42
3M1 30.04.07	M1(J24)	Dry, sunny. The lagoon started to dry. T_{water}= 14.6ºC;	7.2	1350	1460	3.7	6.0	2.0	7.148

RAINWATER SAMPLES TAKEN FROM 08.05.2007 TO 27.05.2007

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg/l	TSS, mg/l	NO_3^- mg/l
08.05.07	Woodbrook	Dry. T_{air} = 16ºC	7.6	350	600	1.13	19.14	10.0	Problems with nitrates (pre-washed bottles with HNO_3)
3M1 11.05.07	M1 (J24)	Cloudy, windy; T_w = 13ºC; depth of water = 35 cm	7.2	820	1630	3.35	9.17	11.0	
b/w 11.05.07	M1(J24)		7.7	1140	2560	6.71	11.29	13.0	
3M1 18.05.07	M1 (J24)	T_w = 18.6ºC.	6.9	550	1130	3.83	8.48	9.0	0.422
b/w 18.05.07	M1 (J24)		7.2	690	1270	28.5	13.51	21.0	Not analysed
Inlet 18.05.07	M1 (J24)	T_w = 16.8ºC.	7.4	`1000	2220	44.1	25.31	83.0	1.672
25.05.07	Woodbrook	T_{air} = 19ºC. Cloudy, dry	7.9	300	550	1.56	3.36	6.0	18.42
27.05.07	Woodbrook	Rain during two days – heavy showers. T_{air} = 10ºC; T_w = 13.5ºC.	6.9	130	260	6.75	12.6	11.0	9.89
27.05.07 duplicate	Woodbrook	T_w = 11.6ºC.	6.7	130	160	6.6	6.88	13.0	9.17

RAINWATER SAMPLES TAKEN FROM 05.10.2007 TO 28.10.2007

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l
05.10.07	Woodbrook	T_w = 10ºC	7.6	330	600	1.8	2.91	30	300	23.32
09.10.07 Inlet	M1 (J24)	Rain during night and morning. Rain gauge was installed at 10.35 am. Very shallow. Oil film on the water surface	6.8	90	180	56.5	15.97	118	75	11.97
b/w 09.10.07	M1 (J24)		7.2	100	210	4.47	5.69	12	60	0
a/w 09.10.07	M1 (J24)		7.4	310	630	3.33	6.13	25	185	0.44
20.10.07	Woodbrook	Dry; shallow	7.7	280	580	1.58	3.25	6	235	21.729

RAINWATER SAMPLES TAKEN FROM 17.12.2007 TO 21.12.2007

Number and date of sample collection	Location	Weather	pH	TDS, mg/L	EC, µs/cm	Turb, NTU	TOC, mg /L C	SS, mg/L	Hardness, tot, mg/L $CaCO_3$	NO_3^- mg/L	PO4
b/w 17.12.07	M1(J24)	The lagoon was frozen. Thickness of the ice was 4-5 cm (3M1). To collect samples it was necessary to break the ice.	6.6	490	930	23.4	5.26	8	137	0.630	0.111
3M1 17.12.07	M1(J24)		6.7	280	630	20.6	6.02	47	115	_	0.485
21.12.2007	Woodbrook	T_w = 3.3 ºC	7.8	290	570	5.37	1.78	16	185	30.442	0.389

RAINWATER SAMPLES TAKEN FROM 03.01.2008 TO 23.01.2008

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l
3M1 03.01.08	M1 (J24)	Windy; T_w = 3.1 ºC	7.5	380	790	7.57	6.13	8	108	0.197	0.892
b/w 03.01.08	M1(J24)	T_w = 1.8 ºC	7.5	590	1250	80.1	7.417	31	130	0.785	0.240
a/w 03.01.08	M1(J24)	Thin cover of ice	7.6	400	820	9.25	6.35	18	155	0	0
15.01.2008	Woodbrook	Heavy shower.	7.3	150	300	183	14.91	105	425	56.491	1.272
16.01.2008	Woodbrook		6.9	170	350	107	13.32	61	265	25.554	0.134
17.01.2008	Woodbrook	Heavy shower	7.4	200	400	35.7	6.12	55	175	25.683	0
22.01.08	Woodbrook	Dry weather. It was raining 21.01.08	7.4	220	440		10.93	14	195	24.569	0.099
23.01.08	Woodbrook	Dry	7.6	240	500	12.9	5.42	12	185	27.212	0

RAINWATER SAMPLES TAKEN FROM 14.04.2008 TO 30.04.2008

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
3M1 14.04.08	M1 (J 24)	Dry	7.0	520	1070	2.49	2.51	14.0	185	0.438	0.208	164.46
b/w 14.04.08	M1 (J24)		7.3	660	1290	5.42	27.37	27.0	80	0.138	0	243.49
			7.1	440	750	2.69	11.39	14.0	122	0.284	0	173.0
a/w 14.04.08	M1 (J24)		7.1	1310	3300	46.4	41.07	126.0	185	0	0	574.14
Inlet 14.04.08	M1 (J24)											
30.04.08	Woodbrook	During night there was a heavy shower	7.8	210	420	15.5	14.71	12.0	165	17.131	0	21.83

RAINWATER SAMPLES TAKEN FROM17.05.2008 TO 30.05.2008

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
17.05.08	Woodbrook	Light drizzle	7.8	280	550	8.42	11.79	15.0	325	20.054	0.609	26.97
27.05.08	Woodbrook	25/05/08 and 26/06/08 it was raining.	7.3	160	320	4.8	10.0	8.0	235	12.961	0.158	12.80
28.05.08	Woodbrook	Heavy rain	7.3	190	400	40.0	25.3	54.0	235	19.196	0.183	17.85
30.05.08	Woodbrook	Rain 29.05.08	7.2	220	430	4.16	13.5	5.0	220	15.792	0.109	15.91
3M1 30.05.08	M1 (J 24)	Rain during night	7.3	410	790	17.6	11.745	39.5	175	1.534	0	127.78
b/w 30.05.08	M1 (J 24)		6.9	190	380	52.9	14.44	31.5	130	2.995	0	63.60
a/w 30.05.08	M1 (J 24)		7.3	300	590	39.6	21.11	45.0	185	2.370	0	90.92
Inlet 30.05.08	M1 (J 24)		7.1	190	370	41.1	15.92	24.0	130	2.585	0	65.38

RAINWATER SAMPLES TAKEN FROM 23.06.2008 TO 30.06.2008

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
23.06.08	Woodbrook	Dry	8.2	310	640	2.79	9.0	9.0	325	18.736	0	18.92
3M1 26.06.08	M1 (J 24)	Dry; shallow; algae	7.7	390	740	2.29	13.01	5.0	122	0.482	0	121.8
b/w 26.06.08	M1 (J 24)		6.9	250	420	6.23	12.23	25.0	115	3.872	0	60.1
a/w 26.06.08	M1 (J 24)		7.9	400	730	2.91	12.55	11.0	102	3.437	0	112.0

RAINWATER SAMPLES TAKEN FROM 11.07.2008 TO 29.07.2008

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
Inlet 13.20 11.07.08	M1 (J24)	There were heavy and light showers throughout this week. One could observe 2 showers on this day. 12.50 – 13.50 – 4 mm; 14.00 – 14.20 – 2 mm. It was also observed how water flowed into the lagoon via the weir.	7.0	190	390	51.7	15.91	24	145	1.948	0	46.04
Inlet 13.40 11.07.08			7.0	130	250	62.1	15.96	39	85	1.217	0	31.75
Inlet 14.00 11.07.08			7.0	110	230	56.7	14.283	125	95	1.244	0	26.00
Inlet (2nd shower) 14.30 11.07.08			6.9	120	240	59.0	13.025	42	137	1.222	0	30.72
Inlet (2nd shower) 14.50 11.07.08			6.9	130	270	59.9	14.36	45	95	1.467	0	32.63
Flowing into the lagoon 14.50			6.8	160	340	12.4	12.31	7	90	0.525	0	40.72
Flowing into the lagoon 15.00			6.7	160	330	11.6	11.89	12	108	1.320	0	39.85
			7.9	2600	5120	2.76	19.65	Not analysed	465	Due to the massive value of chloride (more than 450 ppm), it was impossible to analyse nitrates		Not analysed

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
23.07.08	Woodbrook	Dry. Sunny. Shallow.	7.8	290	570	1.39	6.64	5.34	265	16.612	0.123	9.00
29.07.08 Ch - (upper layers)	M1(J 24)	Dry and sunny. There was no water after the trap. The lagoon is drying. Shower in the morning.	6.9	210	420	4.84	15.83	5.84	130	0.789	0	26.36
29.07.08 Ch - (lower layers)			6.8	210	410	21.9	13.72	36.75	102	0.130	0	45.23

RAINWATER SAMPLES TAKEN FROM 08.09.2008 TO 09.09.2008

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
08.09.08	Woodbrook	Dry, but last night there was heavy rain.	7.1	210	420	9.67	19.08	7.0	175	24.933	0	19.74
Inlet 9.30 09.09.08	M1 (J 24)	*Amount of precipitation from 01.09 to 08.09 - 20 cm.* Rain started approx. at 8 am. Rain gauge was installed upon arrival in the lagoon at 9.30. 9.30 – 9.45 – 1mm 9.45 – 10.00 –few drops 10.00 – rain stopped 10.35 rain started again. 10.35 – 11.00 – drizzle (few drops) 11 – 11.15 – 0.5 mm 11.15 – 11 25 – 0.2 mm	7.1	590	1180	24.2	15.91	22.0	355	2.492	0	96.83
Inlet 9.45 09.09.08			7.0	410	800	90.3	11.72	91.3	Not analysed	3.797	0	47.05
Inlet 10.20 09.09.08			7.0	230	460	102	10.38	129	Not analysed	3.070	0	38.39
b/w 9.30 09.09.08			7.1	630	1240	10.1	12.32	13.75	Not analysed	1.793	0	98.16
b/w 9.45 09.09.08			7.0	540	1080	39.8	13.48	45.0	Not analysed	3.323	0	80.23
b/w 10.00 09.09.08			7.0	410	810	79.6	14.04	76.43	Not analysed	5.341	0	62.74
b/w 10.20 09.09.08			7.0	300	590	102	13.928	105.95	235	3.844	0	44.12
a/w 9.30 09.09.08			7.0	480	880	6.66	11.32	4.75	235	1.566	0	76.13

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
a/w 9.45 09.09.08	M1 (J 24)		7.0	560	1110	10.8	12.43	10.25	390	1.823	0	89.74
a/w 10.00 09.09.08			7.0	540	1060	27.3	9.3	22.5	355	2.535	0	89.78
a/w 10.20 09.09.08			7.0	470	930	45.1	13.51	41.0	500	6.431	0	75.83
a/w 10.45 09.09.08			7.0	390	780	63.3	13.06	37.5	Not analysed	3.732	0	64.43
a/w 11.15 09.09.08			6.8	310	540	75.7	13.778	78.0	Not analysed	3.568	0.080	51.76
a/w 11.35 09.09.08			6.6	310	580	79.0	19.39	81.0	425	3.294	0.409	45.54

RAINWATER SAMPLES TAKEN FROM 28.09.2008 TO 27.11.2008

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
28.09.08	Woodbrook	Dry, shallow	7.0	280	550	1.19	4.25	4.0	325	20.69	0.39	13.48
24.11.08	Woodbrook	23/11/08 there was rain	7.0	240	500	1.38	7.55	5.5	355	24.61	1.52	19.42
25.11.08	Woodbrook	Dry, chilly	7.8	240	480	1.10	5.39	3.0	300	25.34	0.12	17.89
27.11.08 Inlet	M1 (J 24)	Dry, windy	7.5	1570	3600	19.46	9.73	47	500	2.642	0	448
27.11.08 b/w			7.5	380	740	2.91	9.91	12.4	210	0.643	0	81.68
27.11.08 Ch - upper			7.2	430	840	3.12	4.92	4.34	390	0.892	0	86.21
27.11.08 Ch - lower			7.0	430	840	100	6.51	7335	325	0.756	0.47	95.77
27.11.08 a/w			7.3	190	370	1.82	4.723	3.0	122	0	0	51.72
27.11.08 3M1			7.4	180	370	1.42	3.953	4.0	70	0.127	0	53.46

RAINWATER SAMPLES TAKEN FROM 13.12.2008 TO 15.12.2008

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
13.12.08	Woodbrook	Rain started 12.12.2008 evening Water was very turbid.	6.9	130	260	215	25.7	295	n/a	22.881	0.586	15.15
15.12.08 (inlet)	M1 (J 24)	The chamber was full. It was turbid. Rain started 12.12.2008 evening and finished 13.12.2008 in the evening. Trace of ice on the surface of the water	7.4	1430	4020	34.6	5.78	22.67	250	4.950	0	519.4
15.12.08 Ch			7.5	1490	2620	41.4	4.84	28.0	280	3.684	0	390.3
15.12.08 b/w			7.4	970	1880	32.5	3.6	16.0	165	4.471	0	337.2
15.12.08 a/w			7.2	250	490	5.3	3.57	4.5	80	2.527	0	69.83
15.12.08 3M1			7.1	240	490	4.1	5.25	4.0	85	0.127	0	69.87

RAINWATER SAMPLES TAKEN FROM 08.01.2009 TO 27.02.2009

Number and date of sample collection	**Location**	**Weather**	**pH**	**TDS, mg/l**	**EC, µs/cm**	**Turbidity, NTU**	**TOC, mg /l**	**TSS, mg/l**	**Hardness, tot, mg/l $CaCO_3$**	NO_3^- **mg/l**	**PO_4, mg/l, as P**	**Na^+, mg/l**
08.01.09	Woodbrook	Last week the temperature of air was up to -5°C. 07.01.09 there was slight drizzle	7.5	510	1010	7.22	9.08	6.67	425	25.672	0.090	117.74
10.01.09	Woodbrook	Cold, dry, frost on the grass	7.9	200	500	1.18	Not analysed	3.34	355	28.081	0.089	19.33
12.01.09	Woodbrook	Rain. The temperature increased up to 10°C	7.5	260	520	37.2	7.7	25.0	n/a	14.549	0	52.92
13.01.09 (Inlet)	M1 (J 24)	The water was turbid in the inlet and before the weir. The depth of water after weir was 23 cm.	7.3	1170	1420	157	14.683	91.0	265	1.232	0	373.75
13.01.09 Ch			7.2	1290	4170	3.17	6.53	9.0	425	2.02	0	722.77
13.01.09 b/w			7.4	1680	3280	159	10.79	100.0	355	1.304	0	396.00
13.01.09 a/w			7.3	490	950	3.3	4.06	7.0	137	0	0	142.06
13.01.09 3M1			7.1	490	960	2.4	5.76	3.2	Not analysed	0	0	149.96

Number and date of sample collection	**Location**	**Weather**	**pH**	**TDS, mg/L**	**EC, µs/cm**	**Turb, NTU**	**TOC, mg /L C**	**SS, mg/L**	**Hardness, tot, mg/L $CaCO_3$**	NO_3^- **mg/L**	**PO_4, mg/L, as P**	**Na^+, mg/L**
22.01.09	Woodbrook	Rain started 21.01.2009 @ approx. 8 pm	7.05	200	380	66.3	n/a	64.0	Not analysed	20.04	Not analysed	25.51
22.01.09 (inlet)	M1 (J 24)	The water was turbid in the inlet and before the weir. The depth of water after weir is 25 cm. Water was flowing through the weir due to wind.	7.61	1980	3760	221	n/a	164	Not analysed	2.35	Not analysed	655.31
22.01.09 b/w			6.92	1190	2680	53.5	n/a	31	Not analysed	2.71	Not analysed	387.44
22.01.09 b/w' bottom sample			7.38	2560	5550	858	n/a	2716	Not analysed	1.92	Not analysed	n/a
22.01.09 a/w I			7.61	2840	5700	107	n/a	72	Not analysed	2.59	Not analysed	731.79
22.01.09 a/w II			7.53	2200	5100	108	n/a	77	Not analysed	2.17	Not analysed	730.29
22.01.09 a/w III			7.49	2060	3920	112	n/a	75	Not analysed	2.14	Not analysed	704.57
22.01.09 Ch			7.51	1190	1780	43.5	n/a	37	Not analysed	1.88	Not analysed	339.85
22.01.09 3M1			7.44	200	1100	3.98	n/a	5	Not analysed	3.99	Not analysed	173.35
27/02/09	Woodbrook	Dry, windy	7.97	210	440	2.98	7.88	15.0	Not analysed	25.556	0.069	14.106

RAINWATER SAMPLES TAKEN FROM 03.03.2009 TO 21.04.2009

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l;	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
03.03.09	Woodbrook	Light drizzle during night. Samples were taken in the morning	8.05	280	510	4.46	3.87	3.0	280	27.178	0	16.132
03.03.09 (Inlet) 10 cm	M1 (J 24)	Long period of dry weather (2 weeks). Rain started at approx. 2 pm. Samples were collected at 3.20 pm.	7.67	5730	11700	21.2	9.37	50.0	More than 500	0	0	168.34
03.03.09 b/w			7.59	3040	7840	14.3	8.81	49.0	More than 500	3.799	0	882.43
03.03.09 Ch 75 cm			8.23	3480	8500	3.17	5.36	16.5	More than 500	0	0	936.2
03.03.09 b/w' bottom sample 15 ml/50ml			7.13	4320	8600	1116	n/a	n/a	n/a	n/a	n/a	1323.98
03.03.09 a/w 34 cm			7.28	1530	3940	5.97	9.44	6.5	195	2.327	0	550.43
03.03.09 3M1 5 cm			7.39	1520	2800	3.31	3.88	8.0	210	2.151	0	536.41

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
01.04.09	Woodbrook	Dry , sunny, shallow	8.04	290	520	2.02	10.26	18	390	24.06	0	14.154
15.04.09	Woodbrook	Rain during night and morning	7.08	190	380	14.2	21.85	17.5	280	21.634	0.067	20.29
21.04.09	Woodbrook	Dry, shallow, sunny	7.71	300	530	2.63	7.31	29.0	265	23.421	0.072	14.39
21.04.09 Inlet 4 cm	M1 (J 24)	Dry, the lagoon is going down: shallow, covered with reeds.	7.8	1140	2300	44.2	30.24	141.0	265	8.197	0	328.406
21.04.09 Ch			7.95	1900	3220	8.67	12.64	26.0	195	7.129	0	508
21.04.09 a/w 9 cm			7.01	1800	3000	1.84	15.329	24.0	265	4.943	0	500
21.04.09 3M1 7 cm			7.7	1790	3540	2.31	14.246	12.0	220	4.264	0	486.97

RAINWATER SAMPLES TAKEN FROM 12.05.2009 TO 14.05.2009

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
12.05.09	Woodbrook	Dry , sunny, shallow	7.51	290	510	2.09	7.07	5.0	465	24.26	0.105	18.576
14.05.09 b/w	M1 (J24)	Cloudy. Dry.	8.46	1120	1880	20.6	15.62	25.34	165	8.09	6.03	543
14.05.09 Ch			7.8	2440	4000	7.83	7.57	14.34	235	4.35	6.12	591.2
14.05.09 3M1			7.46	2760	4560	2.06	8.03	11.34	250	5.66	0	667

RAINWATER SAMPLES TAKEN FROM 03.07.2009 TO 29.07.2009

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
03.07.09 Ch 8.45 am	M1(J24)	**Very long period of dry weather with very high temperature (~30°C).** **Inlet into the lagoon was dry.** **Water was only in chamber with the level of 48 cm.** 8.44 9.00 0.5 9.15 1.9 9.30 2.9 9.45 4.0 10.00 5.0 10.15 6.0 10.30 6.5 10.45 7.0 11.00 7.5 11.15 8.0 11.30 9.0 11.45 9.1 12.45 Ch =57 Start. again 12.55 13.10 12 13.25 14 13.40 Wind Ch =70 14.1	7.59	480	910	6.41	19.57	16.5	137	5.391	6.588	Not analysed
03.07.09 11.30 am Inlet			7.38	190	400	162	72.063	179.0	137	13.941	6.706	Not analysed
03.07.09 12.15 am b/w			7.28	420	780	23.5	33.77	20.0	115	7.274	7.799	Not analysed
03.07.09 b/w 2pm			7.58	200	380	110	50.59	86.0	145	16.205	6.773	Not analysed
03.07.09 b/w 2.15 pm			7.26	160	260	158	82.855	118.0	95	11.134	6.852	Not analysed
03.07.09 b/w 2.30 pm			7.63	130	270	155	51.581	121.0	165	12.864	6.495	Not analysed
03.07.09 a/w 2pm			7.77	440	850	5.73	34.735	10.5	115	7.751	5.598	Not analysed
03.07.09 a/w 2.15 pm			7.6	350	690	56.1	38.51	49.0	108	10.224	5.524	Not analysed
03.07.09 a/w 2.30 pm			7.55	380	720	42.8	32.35	41.0	137	47.106	1.733	Not analysed

Number and date of sample collection	Location	Weather	pH	TDS, mg/L	EC, µs/cm	Turb, NTU	TOC, mg /L C	SS, mg/L	Hardness, tot, mg/L $CaCO_3$	NO_3^- mg/L	PO_4, mg/L, as P	Na^+, mg/L
07.07.09 11 am	Woodbrook	06/07/09 heavy rain	7.43	270	260	2.55	5.85	10.0	300	12.778	0.664	16.409
07.07.09 4 pm	Woodbrook	Heavy rain during sample collection	6.96	130	510	74.5	69.14	273	265	8.28	0.852	9.35
17/07/09 Inlet 22 cm	M1 (J24)	Wet period since 03/07. Samples were collected during dry weather after the rain	7.07	170	350	54.2	19.3	34	210	7.234	4.622	46.24
17/07/09 b/w			7.09	110	210	12.0	9.265	11	108	7.213	4.576	28.31
17/07/09 Ch 84 cm (nearly over the crest)			7.03	140	280	18.0	29.407	11	115	4.685	5.465	35.0
17/07/09 3M1			7.73	580	1160	0.188	12.3	3	175	23.799	3.7	225.54
20/07/09	Woodbrook	Sample was collected during dry weather. The day before there was some rain.	8.17	290	560	2.27	3.69	13	300	12.423	0.521	19.2
29/07/09	Woodbrook	Heavy rain	7.57	180	390	17.8	27.13	83	280	8.58	2.467	14.85

RAINWATER SAMPLES TAKEN FROM 10.08.2009 TO 28.08.2009

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
10.08.09	Woodbrook	Rainy weather since the middle of July. During sample the weather was dry, although squelch.	7.46	250	480	3.5	9.53	4.21	235	21.445	0.846	16.04
13.08.09	Woodbrook	Dry weather since 10/08. Shallow.	7.21	280	560	2.17	3.45	3.31	250	20.981	0.350	18.18
18/08/09 Chamber 65 cm	M1 (J 24)	Dry and sunny. Suspended solids are presented by algae	7.0	220	430	6.57	7.47	16.5	130	4.493	7.569	49.98
18/08/09 a/w 20 cm			7.45	350	660	2.5	12.71	12.0	108	15.881	5.469	117.32
18/08/09 3M1			7.5	350	640	3.9	9.47	12.5	130	9.688	7.831	111.24
19/08/09	Woodbrook	Dry and shallow	8.07	330	640	1.42	6.69	2.45	250	21.873	0.534	18.51
28/08/09	M1 (J24)	Windy, cloudy Suspended solids are presented by algae	7.5	350	630	2.06	10.928	26.5	60	3.164	0.841	109.54

RAINWATER SAMPLES TAKEN FROM 02.09.2009 TO 29.09.2009

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
02/09/09 Chamber 65 cm	M1 (J24)	Dry; algae	7.19	290	550	5.88	9.01	6.5	102	2.092	0	73.75
02/09/09 3M1			7.29	360	690	4.96	12.275	66	85	2.477	1.566	112.05
03/09/09 Chamber 85 cm	M1(J24)	There was rain last night. Dry; algae	7.23	220	420	27	12.2	19	145	1.878	0	54.3
03/09/09 a/w 6 cm			7.27	260	500	39.1	12.85	192	175	3.277	0	69.96
07/09/09 Chamber 69 cm	M1(J24)	The weather was dry; algae, shallow	7.28	210	410	5.43	20.98	14	90	Not analysed	Not analysed	51.29
07/09/09 a/w 6 cm			8.42	260	520	76.5	62.98	341	115	Not analysed	Not analysed	79.69
09/09/09 Chamber 63.5 cm	M1(J24)	The weather is dry; algae, shallow	7.42	210	410	3.47	6.55	14.5	108	Not analysed	Not analysed	52.05
09/09/09 3M1			7.95	330	650	6.65	11.45	123	70	Not analysed	Not analysed	103.48

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na^+, mg/l
14/09/09 Chamber 59cm	M1 (J24)	Dry; algae	7.2	250	470	6.18	7.09	31.5	122	1.463	0	59.09
14/09/09 3M1			7.00	360	690	15.7	10.94	88	56	2.81	0.98	114.86
16/09/09 Chamber 56.9 cm	M1 (J24)	Dry; algae, shallow sample was taken from the middle of the lagoon	7.95	250	480	9.1	15.13	39	95	1.686	0	63.49
16/09/09 3M1			7.95	350	670	15.4	12.49	23.5	65	2.256	0	113.79
16.09/09	Woodbrook	Shallow	7.95	290	580	0.209	9.13	5.34	390	20.332	0.367	15.38
18/09/09	Woodbrook	Shallow. Dry	8.06	320	600	0.198	4.94	3.0	280	19.922	1.339	16.29
25/09/09 Chamber 49 cm	M1 (J24)	Dry; algae, shallow	7.57	300	550	5.58	7.63	15	115	1.180	0.620	82.38
25/09/09 3M1			7.28	380	730	56.0	9.39	91	108	3.136	1.089	129.09
29/09/09 Chamber 42.5 cm	M1 (J24)	Dry; algae, shallow	7.4	320	620	6.19	7.19	14	115	Not analysed	Not analysed	88.37
29/09/09 3M1			7.04	400	750	146	14.36	161	3003.0	Not analysed	Not analysed	131.45

RAINWATER SAMPLES TAKEN FROM 21.10.2009 TO 29.10.2009

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na, mg/l
21/10/09 Chamber 52.8 cm	M1 (J 24)	Last night there was some rain	7.06	150	260	8.16	20.569	14	95	0.796	0	37.68
21/10/09 3M1 21 cm (middle of the lagoon)			7.09	310	620	57.9	11.74	29	102	1.698	0	106.73
22/10/09 Chamber 52 cm	M1(J 24)	Dry and shallow	7.3	130	250	6.54	10.898	6.5	115	1.143	0.506	36.36
22/10/09 3M1			7.24	270	570	11.6	6.54	7.0	122	1.788	0.914	97.55
29/10/09 Chamber 47 cm	M1(J 24)	Dry and shallow. The lagoon has gone down. No water in the "Inlet"	7.05	210	340	9.92	5.4	25	115	0	0	43.82
29/10/09 3M1 17.5 cm (middle of the lagoon)			6.85	310	610	98.8	8.81	82	115	1.073	0.841	112.34

RAINWATER SAMPLES TAKEN FROM 05.11.2009 TO 24.11.2009

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na, mg/l
	M1 (J 24)	Heavy and light showers since 01/11/09										
05/11/09 Chamber 85 cm (full)			6.76	80	150	25.1	5.72	13	70	Not analysed	Not analysed	19.74
05/11/09 3M1 27 cm (middle of the lagoon)			6.72	190	350	45.6	7.135	33	85	Not analysed	Not analysed	62.94
	M1 (J 24)	Predominantly dry weather; few little showers										
09/11/09 Chamber 70.4 cm			6.82	90	170	17.1	5.253	8.5	130	1.607	0.618	23.26
09/11/09 3M1 24.4 cm			6.81	180	350	43.4	9.141	19.5	85	3.239	0	67.70
	M1 (J 24)	Whole day on the lagoon. Spitting; few drops; rains are predominantly during night time.								n/a	n/a	29.56
10/11/09 Chamber 68 cm			6.7	110	190	13.0	4.42	8.5	Not analysed	Not analysed	Not analysed	Not analysed
10/11/09 3M1 20 cm			6.85	180	350	31.5	6.646	32.5	Not analysed	Not analysed	Not analysed	64.98

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na, mg/l
	M1 (J 24)	Heavy and light showers during night time; Light drizzle, few drops. Sample were taken twice: @10.45 am and 3.45 pm.										
13/11/09 Chamber 85 cm (full) 10.45 am			7.15	100	200	79.4	6.313	70	137	1.472	0	35.25
13/11/09 Chamber 85 cm (full) 3.45 pm			7.0	90	190	67.0	5.592	50	95	1.471	0	32.40
13/11/09 3M1 38 cm (middle of the lagoon) 3.45 pm			7.06	170	320	60.3	12.168	133	115	1.893	0	54.21

Number and date of sample collection	**Location**	**Weather**	**pH**	**TDS, mg/l**	**EC, µs/cm**	**Turbidity, NTU**	**TOC, mg /l**	**TSS, mg/l**	**Hardness, tot, mg/l $CaCO_3$**	**NO_3^- mg/l**	**PO_4, mg/l, as P**	**Na, mg/l**
21/11/09 Inlet 5.15 pm	M1(J24)	Rainfall intensity pm mm 5.15 5.30 0.5 5.45 0.9 6.00 1.0 6.15 1.5 6.30 1.8 6.45 2.0	6.95	230	420	52.3	7.78	119.5	210	0	0	57.25
21/11/09 Inlet 5.30 pm			7.00	230	400	21.11	8.31	15	165	0	0	55.54
21/11/09 Inlet 5.45 pm			7.00	210	400	36.1	6.4	6	145	0	0	57.88
21/11/09 Inlet 6.00 pm			7.04	210	400	23.8	5.85	17	145	0	0	55.41
21/11/09 Inlet 6.15 pm			7.14	210	400	38.9	6.72	43	145	0	0	56.34
21/11/09 Inlet 6.30 pm			7.15	200	400	36.6	7.33	37	185	0	0	55.26
21/11/09 Inlet 6.45 pm			7.12	200	410	35.1	8.66	35	210	0	0	60.49
21/11/09 Chamber 5.15 pm 79 cm			7.2	130	240	23.3	5.046	14	122	1.183	0	38.13
21/11/09 Chamber 6.45 pm 80 cm			7.15	120	240	22.9	6.836	16	115	1.117	0	32.51
21/11/09 3M1 6.45 pm			7.14	150	310	10.2	5.822	12	95	0.707	0	61.59

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na, mg/l
24/11/09 Inlet Oil film on the surface	M1 (J24)	Dry, windy	6.62	200	380	42.6	10.33	21	165	1.01	0	48.21
24/11/09 Chamber 86 cm			6.71	190	360	25.6	16.99	13	145	1.03	0.067	46.28
24/11/09 3M1 44 cm			6.71	170	340	8.74	7.824	5	80	0.630	0.373	55.83

RAINWATER SAMPLES TAKEN FROM 02.12.2009 TO 09.12.2009

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, μs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na, mg/l
02/12/09 Inlet	M1 (J 24)	Light drizzle; the runoff could not be captured; In the previous day the temp was -3°C; de-icer salts on the roads	7.09	200	450	23.6	8.524	19	250	Not analysed	Not analysed	44.56
02/12/09 Chamber 850 mm			6.9	160	360	26.0	8.932	12.5	235	Not analysed	Not analysed	37.17
02/12/09 3M1			6.88	150	340	10.2	9.074	9	102	Not analysed	Not analysed	48.35
07/12/09 Inlet 2pm	M1 (J 24)	Rainfall intensity pm mm 2 0 2.15 0.1 2.30 0.3 2.45 0.7 3 1.0 3.15 1.2 3.30 1.7 3.45 2.0	7.23	230	460	23	3.32	14	195	Not analysed	Not analysed	62.26
07/12/09 Inlet 2.15pm			7.35	190	390	22.3	3.98	11	155	Not analysed	Not analysed	59.37
07/12/09 Inlet 2.30pm			7.27	210	430	23.2	7.57	11.5	175	Not analysed	Not analysed	59.09
07/12/09 Inlet 2.45 pm			7.36	240	480	21.5	10.31	12.5	175	Not analysed	Not analysed	68.7
07/12/09 Inlet 3pm			7.34	230	470	21.5	2.79	9.5	210	Not analysed	Not analysed	65.43
07/12/09 Inlet 3.15pm			7.4	260	510	21.8	3.51	9	238	Not analysed	Not analysed	73.45
07/12/09 Inlet 3.30pm			7.39	290	590	20.0	5.53	9.5	235	Not analysed	Not analysed	83.16

Number and date of sample collection	Location	Weather	pH	TDS, mg/l	EC, µs/cm	Turbidity, NTU	TOC, mg /l	TSS, mg/l	Hardness, tot, mg/l $CaCO_3$	NO_3^- mg/l	PO_4, mg/l, as P	Na, mg/l
07/12/09 Inlet 3.45pm	M1 (J 24)		7.39	360	720	21.9	5.84	9	265	Not analysed	Not analysed	99.43
07/12/09 a/w 2 pm			7.42	200	400	31.7	5.45	9.5	175	Not analysed	Not analysed	53.19
07/12/09 a/w 3 pm			7.45	200	410	34.1	3.72	24	175	Not analysed	Not analysed	57.08
07/12/09 a/w 3.45 pm			7.45	200	400	37.2	3.19	27	185	Not analysed	Not analysed	53.74
09/12/09 Inlet	M1(J 24)	Dry	7.09	710	1360	20.9	9.72	12	500	Not analysed	Not analysed	164.55
09/12/09 chamber			7.33	520	1010	30.6	7.84	15.5	500	Not analysed	Not analysed	117.67
09/12/09 3M1			7.23	210	390	10.2	5.86	5	102	Not analysed	Not analysed	63.63

inlet (sample point N 1, see Fig. 4.2); b/w – before weir (sample point N 2, see Fig. 4.2); a/w - after weir (sample point N 3, see Fig. 4.2); 3M1 – sample point N 4 (see Fig. 4.2); ch – chamber (see Photo 4.3 and Fig. 4.3).