June 2009

STYX INTEGRATED CATCHMENT MANAGEMENT PLAN

Styx River Sediment Study

Submitted to:
Christchurch City Council

Report Number: 087813152

REPORT

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COMMON ABBREVIATIONS

µm	Micro-metre
As	Arsenic
ANZECC	Australian and New Zealand Environment Conservation Council
BAP	Benzo[a]pyrene
°C	Celcius (degrees)
Cd	Cadmium
Cr	Chromium
Cu	Copper
ER-L	Effects range low
ER-M	Effects range median
GC-MS-SIM	gas chromatography, mass selective detection, selected ion mode
GPS	Global positioning system
ICMP	Integrated catchment management plan
ICP-MS	Inductively coupled plasma mass spectrometry
ISQG	Interim sediment quality guideline
ISQG-low	Guideline below which adverse toxic effects to biota are unlikely
ISQG-high	Guideline above which adverse toxic effects to biota are probable
JMP	Statistical software package produced by the SAS Institute
mg/kg	Milligrams per kilogram
mm	Millimetre
Ni	Nickel
PAH(s)	Polycyclic aromatic hydrocarbon(s)
Pb	Lead
QMCI	Quantitative macroinvertebrate community index
SAGYRE	Saline gley recent (soils)
SW	South West
TOC	Total organic carbon
USEPA	United States Environmental Protection Agency
YBS	Yellow-brown sand
Zn	Zinc

1.0 INTRODUCTION

1.1 Background

Christchurch City Council (CCC) is developing an Integrated Catchment Management Plan (ICMP) for the Styx River and Wilsons Drain (Styx ICMP area) catchments (Figure 1). This catchment includes the urbanised area of Belfast, for which an area plan is currently being developed. The ICMP process includes the review of existing information, gathering of information to fill identified gaps and assessment of information in terms of integrated catchment management and effects of urban development.

The results of the sediment survey will be used to establish current sediment quality to identify any issues relating to existing contaminant levels that may require specific management measures or specific attention to key contaminants in relation to water quality mitigation.

1.2 Report and Study Scope

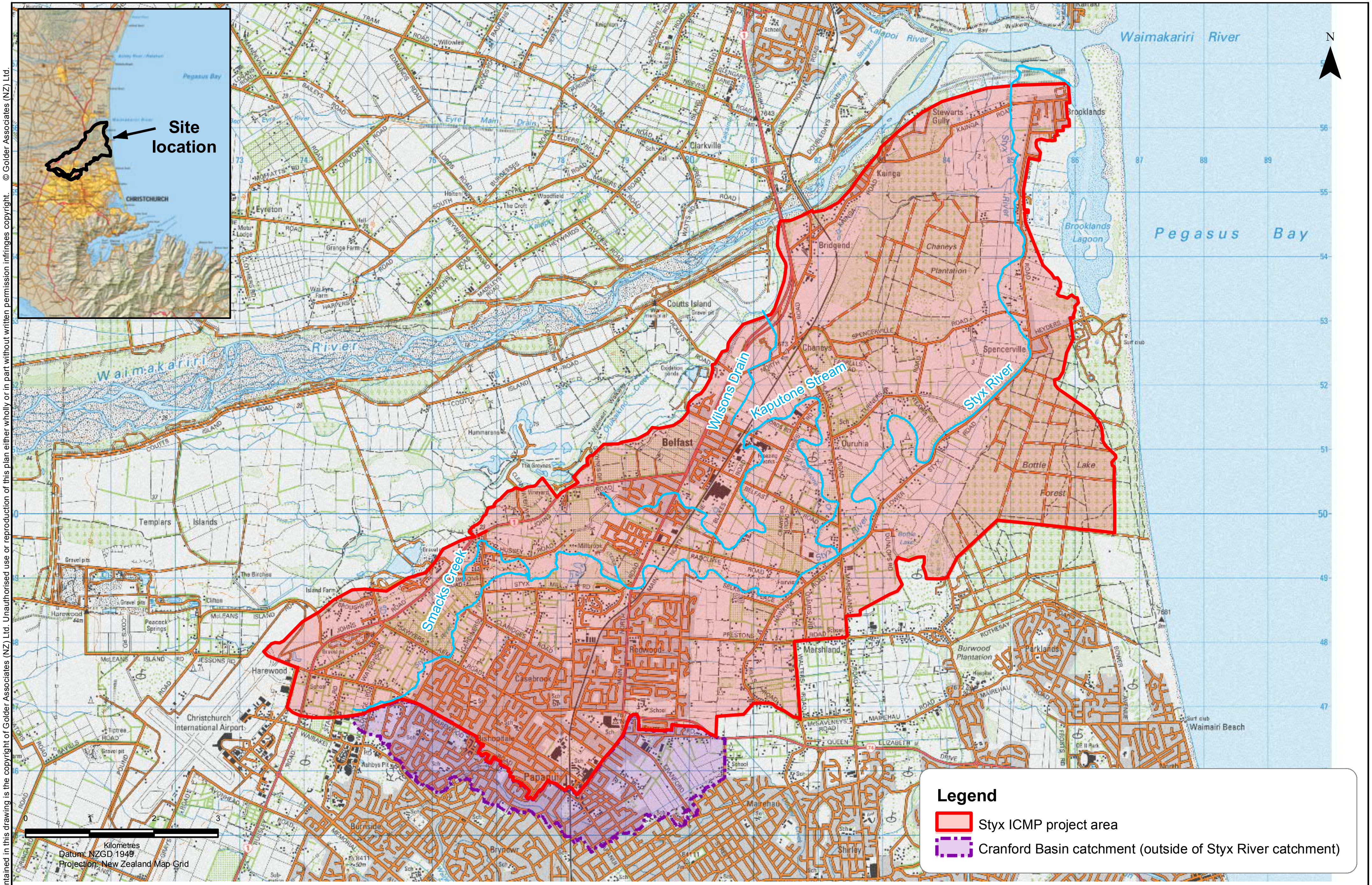
The scope of the sediment survey comprises:

1) A review of previous relevant sediment quality information for Christchurch including the Styx ICMP area and South West Christchurch. This includes a review of the data reported by Robb (1988) and any recent data acquired by CCC or Environment Canterbury; and a summary of issues, trends and knowledge obtained from the South West Christchurch sediment survey.
2) An explanation of of sampling sites within the study catchment, sample collection and laboratory analysis. Initially laboratory analysis to include metals, texture, particle size and screening of polycyclic aromatic hydrocarbons (PAHs) in 10 samples only.
3) Data analysis, interpretation and reporting, including comparisons to sediment quality guidelines, historical data for the Styx, data for other locations in Christchurch and New Zealand. In addition, results to be interpreted with respect to results for aquatic ecology (e.g., Boffa Miskell 2007).
4) Recommendations for catchment management and further monitoring.

This report identifies the location of the study sites, the methods of sampling, historical data and analysis and includes all raw results. It provides interpretation of results including comparisons with Robb (1988). The survey was targeted on the impacts of urbanisation on sediment quality. Contaminants typically associated with urban land use were assessed by the survey rather than contaminants more typically sourced from rural areas, such as pesticides and agricultural chemicals. A further comparison with similar studies in other regions provides an indication of how sediments in the Styx ICMP area compare with those in waterways in South West Christchurch and other New Zealand cities.

The Styx ICMP area in this report includes the Styx River Catchment in addition to the Wilsons Drain site, which lies within an adjoining catchment.

Sediment quality was assessed using the Australian and New Zealand interim sediment quality guidelines (ISQG) for fresh and marine water quality (ANZECC 2000).



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2.0 BACKGROUND INFORMATION ON SEDIMENT QUALITY ASSESSMENT

2.1 Introduction

This section provides background information on factors that affect the physical and chemical characteristics of stream sediment quality, such as geology and stormwater runoff. The sediment in any section of a stream reflects three key factors. These are:

1. The geological nature of the soils and rocks in the catchment (this determines the propensity for weathering and erosion and the texture and mineral composition of the particles).
2. The flow in the stream (i.e., whether it is a depositional (low-energy) or active section (high-energy) of the stream. Fine sediments will accumulate in the depositional sections of streams).
3. The contributions from man-made sources (this depends on the land use in the catchment and discharges of stormwater).

2.2 Geology and Soils

2.2.1 Geology

The underlying geology of the Styx ICMP area belongs to the Yaldhurst member of the Springston Formation, a depositional sequence dominated by unconsolidated sediment accumulating after post glacial marine transgression. The majority of the ICMP area is built on the youngest post-glacial fan surface of the Waimakariri River and is dominated by alluvial sand and silt overbank deposits. The eastern end of the ICMP area also has drained peat swamps belonging to the Yaldhurst and sand and semi-fixed to fixed dunes and beaches belonging to the Christchurch Formation.

2.2.2 Soils and Soil Quality

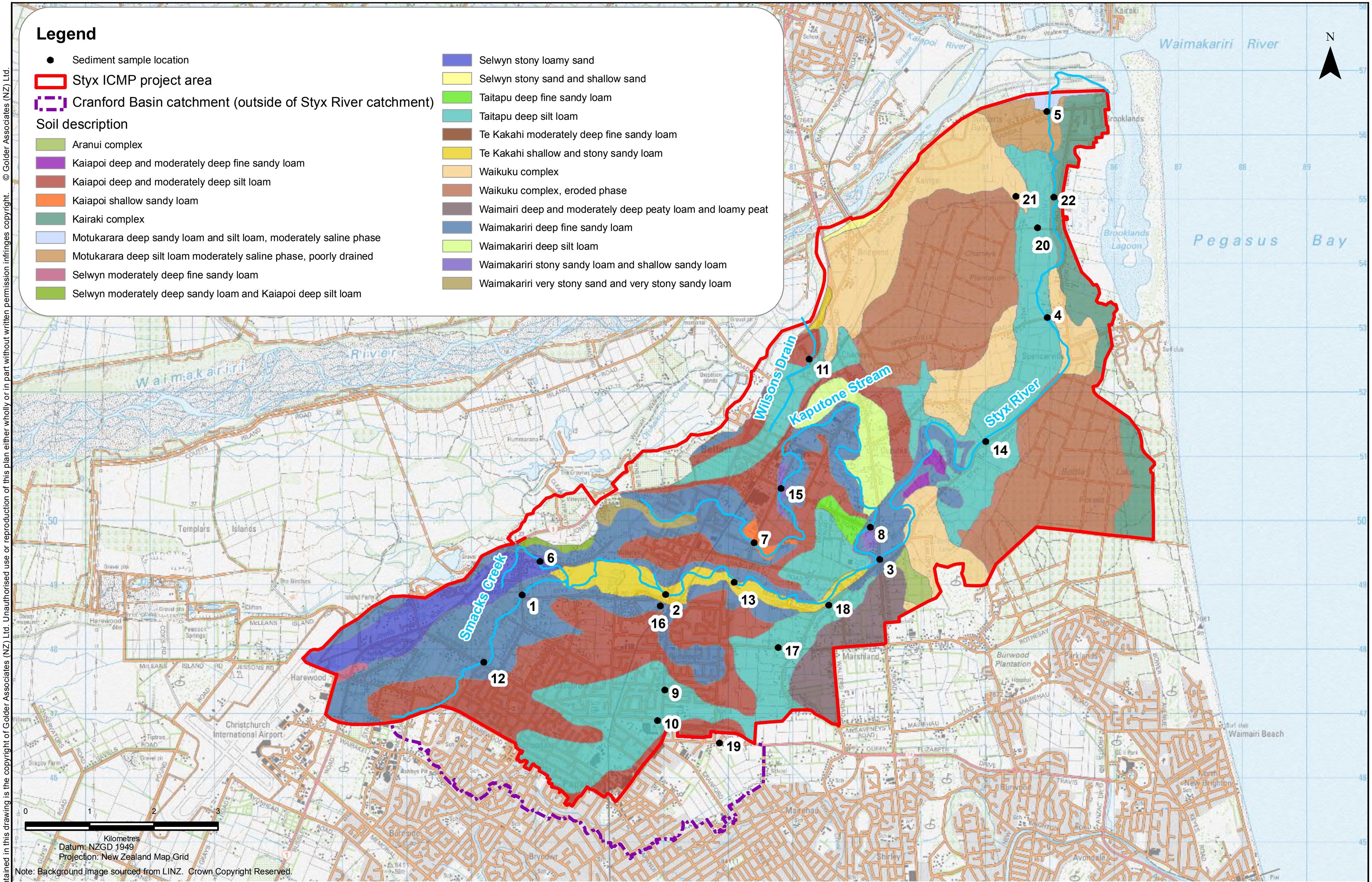
Soils in the Styx ICMP area are predominantly recent soils (Figure 2), with an area of gley soil around Redwood and extending to the north and south along Hills Road. There is an isolated area of organic soils in the horticultural areas near Marshlands Road. To the east of Marshlands Road and extending to the coastline, the soil type is predominantly yellow brown sand (YBS). Soils are described as saline gley recent (SAGYRE) in vicinity of the Styx River mouth.

Trace element concentrations in soil samples have been measured for the soil types described above by previous studies in the area (Tonkin & Taylor 2007a). The maximum concentrations are presented in Table 1. Samples collected from the Christchurch urban area are reported separately.

Table 1: Trace element concentrations in soil types found in the Styx ICMP area.

Soil Region	Regional	Regional	Regional	Regional	Christchurch urban	Christchurch urban
Soil Group	Recent	Gley	YBS	SAGYRE	Recent	Gley
No. of samples	18	6	4	4	8	6
Arsenic	11.5	8.7	3.4	6.8	15.3	10.6
Cadmium	0.18	0.24	0.06	0.09	0.2	0.2
Chromium	20.8	16.8	11	13.2	19	18.5
Copper	18.8	15.5	7.1	12.2	17.7	23.3
Lead	37.4	17.8	31.9	44.4	101	34.9 (127)
Nickel	19	13.4	8.7	9.6	16.6	15.6
Zinc	86.5	65.6	50.7	47.3	149	138

All concentrations are mg/kg.



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2.3 Stormwater and Processes Affecting Sediment Quality

The quality of freshwater sediments in drains and streams generally reflects catchment activities, adjacent activities and the influence of materials placed directly into the stream. In particular, urban runoff typically results in increases in the concentration of common metals such as copper, lead and zinc and PAHs in stream sediments.

Different activities throughout the catchment will result in different materials and contaminants being present on the surface and available for transport to the stormwater system or directly to streams. Stormwater quality therefore (i.e., the types of contaminants present and their load) differs between parks, residential areas, commercial and industrial areas of land and relates to a complex interplay of anthropogenic variables including the types of industry in the adjacent catchment; the density of vehicles on roads in the catchment; the nature and aerial extent of roof surfaces (e.g., whether they are galvanised iron, concrete, tile or other materials); and the deposition of contaminants to land from activities discharging to air (house fires, vehicle emissions and industrial air discharges).

Table 2: Sources of contaminants in urban areas.

Contaminant	Sources
Copper	Road runoff - commonly used in brake linings
Lead	Historical contamination – petrol additive Road runoff - used to minor extent in brake linings
Zinc	Road runoff - used in tyres Roof runoff – used in galvanised roof products
PAHs	Combustion - household fires, industrial emissions, rural burn-offs Vehicle emissions - exhaust, oil and grease leaks, tyre wear Road wear – bitumen and tar

2.4 Sediment Quality Guidelines

The Australian and New Zealand guidelines for fresh and marine water quality (ANZECC 2000) provide interim sediment quality guidelines for metals and PAHs (and other contaminants) in both marine and freshwater environments (Table 3). These are provided as two values, the ISQG-low (interim sediment quality guideline-low) and ISQG-high. The guidelines are trigger values that if exceeded, prompt further action such as evaluation of bioavailability and background concentrations. Where the sediment concentration is below the ISQG-low, it is considered that there is low risk of adverse effects to aquatic species inhabiting the stream sediments.

Table 3: Sediment quality guidelines for metals, metalloids and PAHs (ANZECC 2000).

Contaminant	ISQG-Low	ISQG-High
Metals (mg/kg)		
Arsenic	20	70
Cadmium	1.5	10
Chromium	80	370
Copper	65	270
Lead	50	220
Nickel	21	52

Contaminant	ISQG-Low	ISQG-High
Zinc	200	410
PAHs [a] (mg/kg)		
Acenapthene	0.016	0.50
Acenapthalene	0.044	0.64
Anthracene	0.085	1.10
Fluorene	0.019	0.54
Naphthalene	0.160	2.10
Phenanthrene	0.240	1.50
Low Molecular Weight PAHs [b]	0.552	3.16
Benzo(a)anthracene	0.261	1.6
Benzo(a)pyrene	0.430	1.6
Dibenzo(a,h)anthracene	0.063	0.26
Chrysene	0.384	2.8
Fluoranthene	0.600	5.1
Pyrene	0.665	2.6
High Molecular Weight PAHs [c]	1.7	9.6
Total PAHs	4.0	45.0

Notes: [a] Normalised to 1% organic carbon; [b] Sum of concentrations of acenapthene, acenapthalene, anthracene, fluorene, 2-methylnaphthalene, naphthalene and phenanthrene; [c] Sum of concentrations of benzo(a)anthracene, benzo(a)pyrene, dibenzo(a,h)anthracene, chrysene, fluoranthene and pyrene.

The ANZECC (2000) trigger values are based on sediment guidelines developed by Long et al. (1995). Their guidelines were based on data collected from several hundred sites across the United States as part of the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends Program. The upper and lower guidelines were calculated from the chemical concentrations observed and predicted to be associated with adverse biological effects. The Effects Range Low (ER-L) is the 10-percentile concentration and the Effects Range Median (ER-M) is the median contaminant concentration. The ISQG-Low is based on the ER-L and the ISQG-High is based on the ER-M. Guidelines for some parameters were amended based on other sediment quality guidelines used around the world.

The ANZECC (2000) trigger values, although based on coastal benthic species sensitivity to contaminants, are considered to be suitable as a generic indicator of potential for effects to freshwater biota from sediment quality in freshwater streams.

3.0 REVIEW OF RELEVANT SEDIMENT DATA

3.1 Introduction

This section provides an overview of freshwater sediment data previously collected in the Styx ICMP area, in Canterbury, and around New Zealand. Sediments from estuarine and coastal environments in Canterbury have also been examined in several studies.

3.2 Historical Sediment Quality in the Styx ICMP area

The only previous study of sediment quality in the Styx ICMP area was a study by the Christchurch Drainage Board conducted between November 1980 and February 1981 (Robb 1988). The study reported on the quality of sediments in the Styx River, Kaputone Stream and a number of stormwater and roadside drains (as well as investigating the Avon and Heathcote River catchments, see Section 3.3.2). The surface 10 mm of sediment was collected from the stream or river beds, sieved to 2 mm and analysed for cadmium, chromium, copper, lead, nickel and zinc. The sampling locations used by Robb (1988) are shown in Table 9.

3.3 Sediment Studies in and around Christchurch

3.3.1 South-west Christchurch

Sediment quality was measured as part of background investigations for the South West Christchurch ICMP process. Copper, lead and zinc were measured in surface sediment samples collected from 27 sites in the Heathcote River catchment and 19 sites in the Halswell River catchment (Kingett Mitchell 2005). Higher metal concentrations were typically measured in locations with urban (residential or industrial) land use in the catchment compared to locations with rural land use. Furthermore, zinc concentrations regularly exceeded the ISQG-low and ISQG-high, with the exception of samples collected from rural areas.

The results of this study indicated an increase in zinc concentrations at many locations when compared to the data reported by Robb (1988). In contrast, there was a decrease in lead concentrations at many locations (Kingett Mitchell 2005), consistent with decreases in lead concentrations observed in urban stormwater, associated with the removal of lead from petrol in New Zealand (Kennedy 2003a). This study demonstrated that although the analytical methods used in each study were different, the results were comparable (Kingett Mitchell 2005).

3.3.2 Avon and Heathcote Rivers

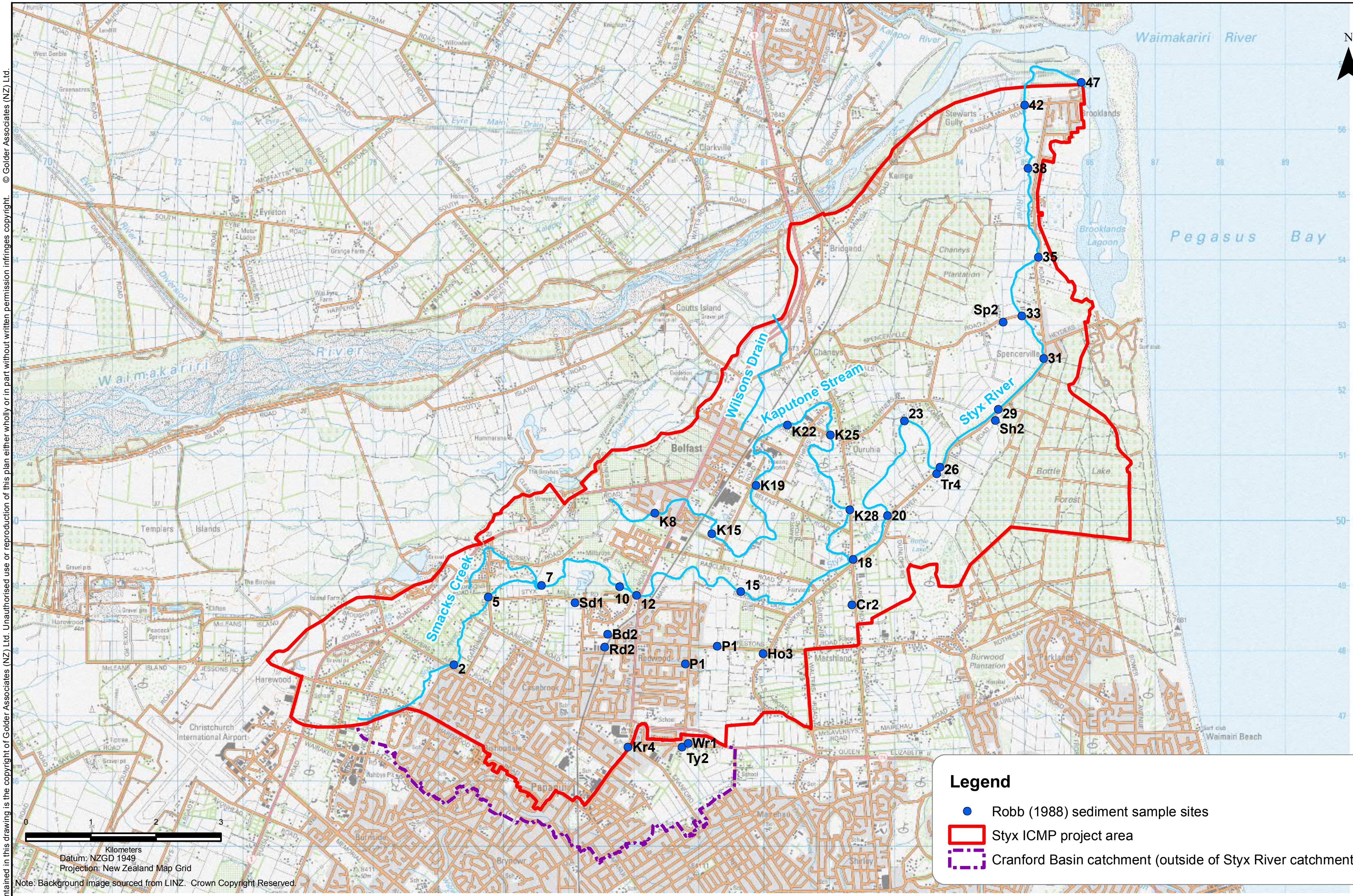
The Christchurch Drainage Board study also investigated sediments in the Avon and Heathcote River catchments, the Avon-Heathcote Estuary and Saltwater Creek Estuary (Robb 1988). The sediments in these rivers contained metals at significantly higher concentrations than sediments collected from the Styx ICMP area. Lead concentrations were highest in sediments from the Avon River, which received a greater volume of road runoff than the Heathcote or Styx Rivers (Robb 1988). In many of the urban locations, the concentrations of zinc and lead exceeded ANZECC (2000) guidelines.

3.3.3 Rangiora waterways

Sediment quality has been studied in North, Middle and South Brooks of Rangiora (Golder 2008; Main & Lavender 2003), the Cam River (Main & Lavender 2003) and in drains around the Southbrook Business Zone (Kingett Mitchell 2004a). These studies indicated generally high sediment quality, with few samples exceeding ANZECC (2000) guidelines.

3.4 Estuarine and Marine Sediment Studies

Previous studies of estuarine and marine sediment quality within Canterbury provide a large amount of data that may be used for comparative purposes. These sediments are comparable to the those sampled in the Styx ICMP area as they are have also been derived from rocks such as greywackes and argillites eroded from the Southern Alps, so contain metal concentrations that are representative of their common natural origin.



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3.4.1 Avon-Heathcote Estuary

The sediments of the Avon-Heathcote Estuary have been investigated in multiple studies including the following:

- Measurement of arsenic, cadmium, copper, chromium, lead, nickel and zinc in 10 samples from 7 different locations in the Avon-Heathcote Estuary (Bolton-Ritchie 2008).
- Measurement of arsenic, cadmium, copper, chromium, mercury, nickel, lead and zinc; in four areas of the estuary by Milne (1998).
- Assessment of metal concentrations in, and toxicity of, sediment samples from the estuary and the Heathcote River mouth (NIWA 1997).
- Measurement of cadmium, copper, chromium, nickel, lead and zinc; organic carbon; sediment texture (silt, clay, sand, gravel) at 330 locations across 16 transects by the Christchurch Drainage Board (Robb 1988).
- Measurement of copper, lead and zinc in different size fractions of sediment cores from the estuary by Deely (1988).
- Investigation of organochlorines and PAHs in sediments (Thompson & Davies 1993).

3.4.2 Marine sediment quality

Sediments in Pegasus Bay may be of use in examining the results for the Styx ICMP area. These sediments have been examined in baseline environmental surveys for the Waimakariri District Council's wastewater ocean outfall and for CCC's wastewater ocean outfall.

4.0 METHODOLOGY

4.1 Site Locations

The sampling sites were selected based on the following factors:

- Co-location with other long-term monitoring sites, such as CCC water quality monitoring sites;
- Availability of previous data (Robb 1988);
- To allow comparison between different land use;
- To geographically cover the project area.

The locations of the sampling sites are shown in Figure 4 and described in Table 4. Initially a sample was to be collected from the Railway Drain, downstream of Sturrocks Road; however, due to the nature of this drain (a round concrete pipe), there was insufficient sediment deposited in this area to collect a sample for analysis.

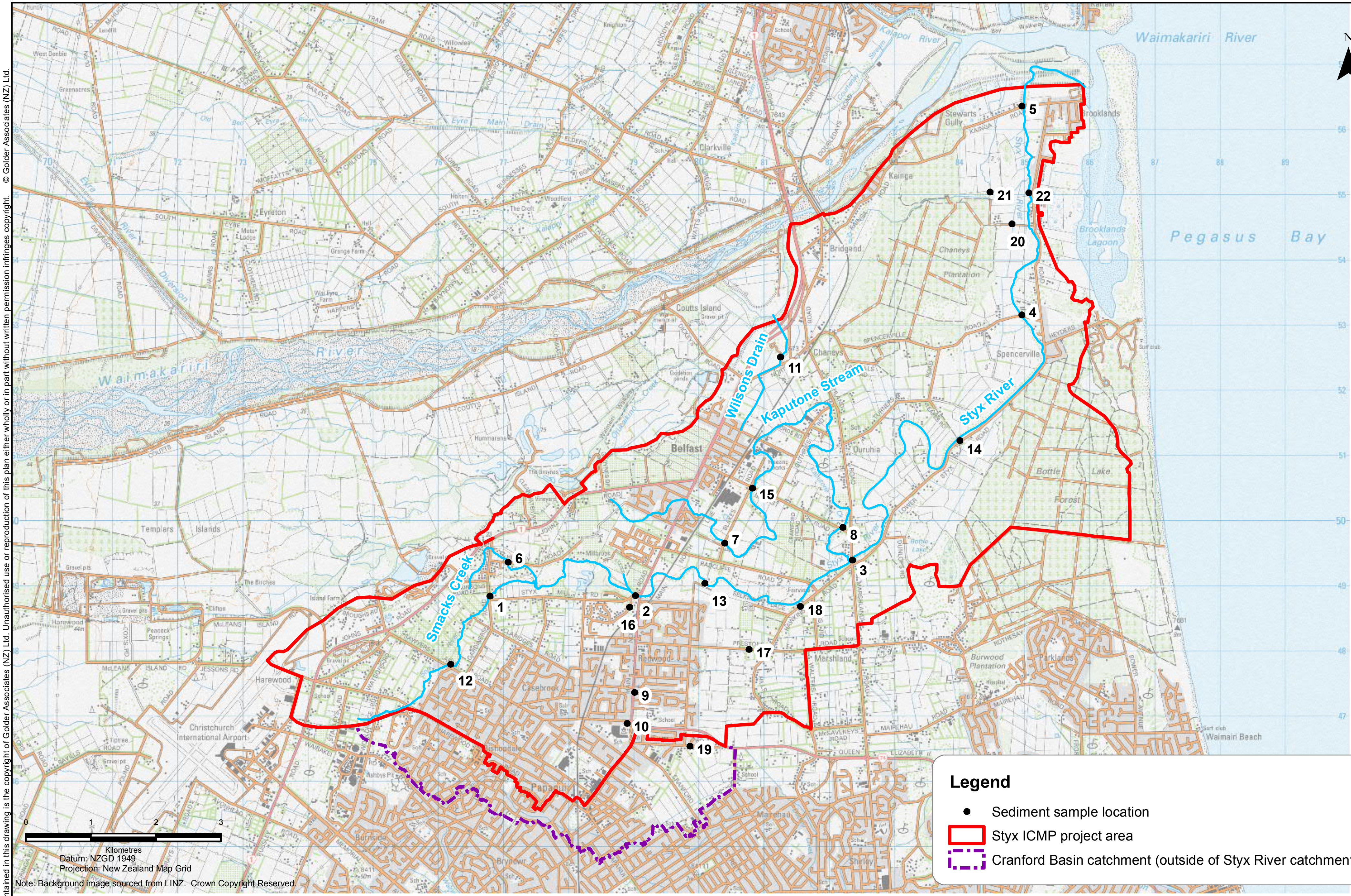

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Table 4: Description of sediment sampling locations in the Styx ICMP area.

Site No.	Waterway	Easting	Northing	Description of location
1	Styx River	2476791	5748845	Gardiners Road
2	Styx River	2479110	5748827	Main North Road
3	Styx River	2482364	5749401	Marshlands Road
4	Styx River	2484964	5753154	Spencerville Road
5	Styx River	2485009	5756361	Kainga Road
6	Smacks Creek	2477072	5749363	Upstream of Husseys Road
7	Kaputone Stream	2480384	5749665	Blakes Road
8	Kaputone Stream	2482200	5749890	Belfast Road east
9	Unnamed Drain	2479015	5747361	Main North Road, between Wingate Street and Momorangi Crescent
10	Kruses Drain	2478900	5746887	Upstream of Main North Road, adjacent to Trents.
11	Wilsons Drain	2481259	5752508	Otukaikino Memorial Reserve
12	Styx River	2476194	5747792	Sawyers Arms Road
13	Styx River	2480092	5749035	Redwood Springs
14	Styx River	2484011	5751224	Teapes Bridge
15	Kaputone Stream	2480824	5750494	Near junction of Belfast and Blakes Roads
16	Styx Drain	2478941	5748670	Stormwater pond adjacent to Regent Park Drive
17	Horners Drain	2480777	5748019	Adjacent to Prestons Road
18	Rhodes Drain	2481563	5748681	Upstream of Hawkins Road
19	Winters Drain	2479864	5746537	Winters Road, downstream of Tysons Drain
20	Spencerville Drain	2484813	5754554	Upstream of small bridge on Earlham Street
21	Kainga Drain	2484477	5755040	Downstream of farm track at end of Earlham Street
22	Styx River	2485070	5755029	Lower Styx Road upstream of Kainga Drain

4.2 Sample Collection

Samples were collected at each site within a slow flowing area and upstream of any obvious point sources such as stormwater pipes (site photographs are presented in Appendix B). Core samples were collected to a depth of 20 to 30 mm using plastic box corers with an area of 60 cm^2. The sampling aimed to collect sediment that was texturally similar between sites. Fine sediments (<2 mm) were preferentially collected to ensure there was sufficient material for laboratory analysis. At least five individual core samples were collected from each site and combined to form a composite sample. The composite sample was homogenised and sub-samples required for the different analytical laboratories were then taken from this sample. Samples were stored in a chilly bin on ice during transport.

At each sampling location a field sheet was completed describing the site characteristics and the presence of upstream discharges. GPS co-ordinates were recorded at each site and photographs were taken of the general stream environment and of the stream-bed (where visible through the water).

All samples were sent to R J Hill Laboratories Limited (Hamilton) under chain of custody.

4.3 Laboratory Analysis

4.3.1 Overall approach

Samples were submitted for analysis in two sequential phases. Samples from sites 1-11 were submitted for analysis by the laboratory (Phase 1), while samples from the remaining sites were held (Phase 2). Samples from sites 12 and 13 were also analysed due to an error by the laboratory. The lab results for samples from sites 1-13 were reviewed and recommended further analysis was identified and discussed with CCC. Samples from sites 14, 15, 17, 18, 20 and 22 were analysed because they were adjacent (upstream or downstream) to Phase 1 sites that had elevated metals concentrations or were representative of rural land use. Table 5 summarises the analyses undertaken on each sample.

Table 5: Summary of analyses undertaken on each sediment sample.

Site No.	Waterway	Analyses undertaken	Rationale
1	Styx River	Particle size, metals, TOC, PAHs	Phase 1
2	Styx River	Particle size, metals, TOC, PAHs	Phase 1
3	Styx River	Particle size, metals, TOC, PAHs	Phase 1
4	Styx River	Particle size, metals, TOC, PAHs	Phase 1
5	Styx River	Particle size, metals, TOC, PAHs	Phase 1
6	Smacks Creek	Particle size, metals, TOC, PAHs	Phase 1
7	Kaputone Stream	Particle size, metals, TOC, PAHs	Phase 1
8	Kaputone Stream	Particle size, metals, TOC, PAHs	Phase 1
9	Unnamed Drain	Particle size, metals, TOC, PAHs	Phase 1
10	Kruses Drain	Particle size, metals, TOC, PAHs	Phase 1
11	Wilsons Drain	Particle size, metals, TOC, PAHs	Phase 1
12	Styx River	Particle size, metals, TOC, PAHs	Phase 2 (lab error - analysed with Phase 1)
13	Styx River	Particle size, metals, TOC, PAHs	Phase 2 (lab error - analysed with Phase 1)
14	Styx River	Particle size, metals, TOC, PAHs	Phase 2 - Upstream of site with elevated results
15	Kaputone Stream	Particle size, metals	Phase 2 - Between sites with elevated metals
16	Styx Drain	Not analysed	Not analysed
17	Horners Drain	Particle size, metals, TOC, PAHs	Phase 2 - Downstream of sites with elevated results
18	Rhodes Drain	Particle size, metals, TOC, PAHs	Phase 2 - Representative of rural land use
19	Winters Drain	Not analysed	Not analysed
20	Spencerville Drain	Particle size, metals, TOC, PAHs	Phase 2 - Representative of rural land use
21	Kainga Drain	Not analysed	Not analysed
22	Styx River	Particle size, metals, TOC, PAHs	Phase 2 - Upstream of site with elevated results

4.3.2 Particle size analysis

Sediments were classified based on their grain size by determining the percentage by weight of particles within the different size ranges. Wet sieving over 2,000 µm and 63 µm, then gravimetric measurement after drying at 103 °C was used for metals analysis (the <2 mm fraction).

Particle size analysis of the smallest fraction was conducted by the Earth Sciences Department of Waikato University, Hamilton. A Malvern Laser Sizer instrument was used to measure a size range of 0.02 to 2,000 µm. Water was used as a dispersant.

4.3.3 Metals

Analysis of sediments for metals can be conducted using a variety of methods, which vary depending on the fraction of sediment analysed, the digestion method used and the instrumental method used. Analysis of different sediment fractions often result in the large differences seen in the final results reported in different studies. This survey and the South-West Christchurch Integrated Catchment Management Plan (Kingett Mitchell 2005) used the USEPA 200.2 method, where samples are digested with nitric acid and hydrochloric acid for 30 minutes at 85 ºC. Previous studies in the Styx catchment (Robb 1988) and for the South-West Christchurch survey analysed the whole sediment sample after removal of >2 mm particles. The same fraction has been used in the current survey.

Different sample digestion methods can also affect the results, with stronger digestion methods typically resulting in higher concentrations. Robb (1988) used a perchloric acid/nitric acid digestion (2.5 mL/4.0 mL for 2 hours) which is not commonly used today. A comparison of the two methods (Kingett Mitchell 2005) showed that similar results were achieved with both digestion methods and that data obtained using the different methods can be reliably compared.

The arsenic and the metals cadmium, chromium, copper, lead, nickel and zinc) were analysed by ICP-MS following total recoverable digestion of dried samples (air dried at 35°C) by the USEPA 200.2 method as described above. All results are presented as mg/kg of dried sediment.

4.3.4 Polycyclic aromatic hydrocarbons and total organic carbon

Samples were analysed for PAHs and total organic carbon (TOC). Total organic carbon analysis was by combustion following acid pre-treatment to remove carbonates.

Samples for PAH screening were extracted by sonication and extracts were either diluted or cleaned up using solid phase extraction if required. Quantitative analysis of PAHs was carried out by capillary gas chromatography using mass selective detection in selected ion mode (GC-MS-SIM). All PAH results are presented as mg/kg of dried sediment.

4.4 Data Analysis and Statistics

Differences between particle size and contaminant concentrations were initially investigated using JMP Version 5.0.1 (SAS Institute). Confidence intervals were also calculated from estuarine and marine sediment data using JMP for comparison to the Styx sediments.

5.0 PHYSICAL CHARACTERISTICS OF SEDIMENT

5.1 Introduction

This section of the report examines the physical characteristics of the sediments collected from the Styx ICMP area. The sediment texture data from samples collected by Robb (1988) and in this survey are presented. It should be noted when reading this section that the particle size data provided is for samples as collected. Although the sediments sampled were selected in the field to emphasise fine sediments required for analysis, the results are still considered to reflect general stream sediment physical characteristics.

5.2 Particle Size

Sediments can be classified with textures that are based on their particle size. A modification of the Wentworth scale has been used in this study (Table 6). Particle size was assessed both by sieving and by laser analysis as described in Section 4.3.2. The laser particle size analysis provided greater information, particularly for comparison with the South-West Christchurch data and this data is used throughout this report. Data from the sieve analysis is detailed in Appendix C and particle size information is detailed in Appendix D.

In most of the waterways, the particle texture was dominated by mud (silt and clay) or fine sand (Figure 5). This may be partly due to deliberate sampling of fine sediments to ensure adequate material less than 2,000 µm in size was available for analysis. Despite this, there appear to be a few differences between samples that are of note:

- The sample from Horners Drain (site 17) had the highest proportion of silt and clay of all samples, at 81%.
- The sample from the unnamed drain (site 9) had the highest proportion of coarse sand at over 50%, substantially higher than that of any other sample.
- Of samples from the main stem of the Styx River, samples from sites 2 and 22 had substantially lower proportions of silt and clay (9% and 8% respectively) than other samples (19-53%).
- The remaining samples from the Styx River mainstem were predominantly made up of very fine, fine and medium sands.

Table 6: Sediment sample texture as measured by particle size analyser.

Waterway	Site No.	Silt and clay (< 63 µm)	Very fine and fine sand (63 - 250 µm)	Medium sand (250 - 500 µm)	Coarse and very coarse sand (500 – 2,000 µm)
Styx	12	40.53	41.41	9.39	8.66
Styx	1	25.41	58.84	10.74	4.99
Styx	2	9.49	67.91	21.66	0.94
Styx	13	47.96	38.15	8.31	5.59
Styx	3	25.90	56.58	17.11	0.40
Styx	14	49.94	40.99	8.23	1.85
Styx	4	53.42	36.19	7.76	2.63
Styx	22	8.32	60.46	30.63	0.59
Styx	5	19.44	44.28	30.18	6.11
Smacks	6	43.95	29.18	12.49	14.40
Kaputone	7	40.43	38.53	10.60	10.41
Kaputone	8	9.51	74.93	15.55	0.00
Kaputone	15	46.68	35.40	8.73	9.21
Unnamed	9	9.32	17.73	19.37	53.60
Kruses	10	7.77	74.85	17.39	0.01
Wilsons	11	67.37	21.70	4.63	6.30
Horners	17	81.02	15.38	2.56	1.07
Rhodes	18	56.23	28.53	9.04	6.22
Spencerville	20	59.42	31.78	7.79	1.02

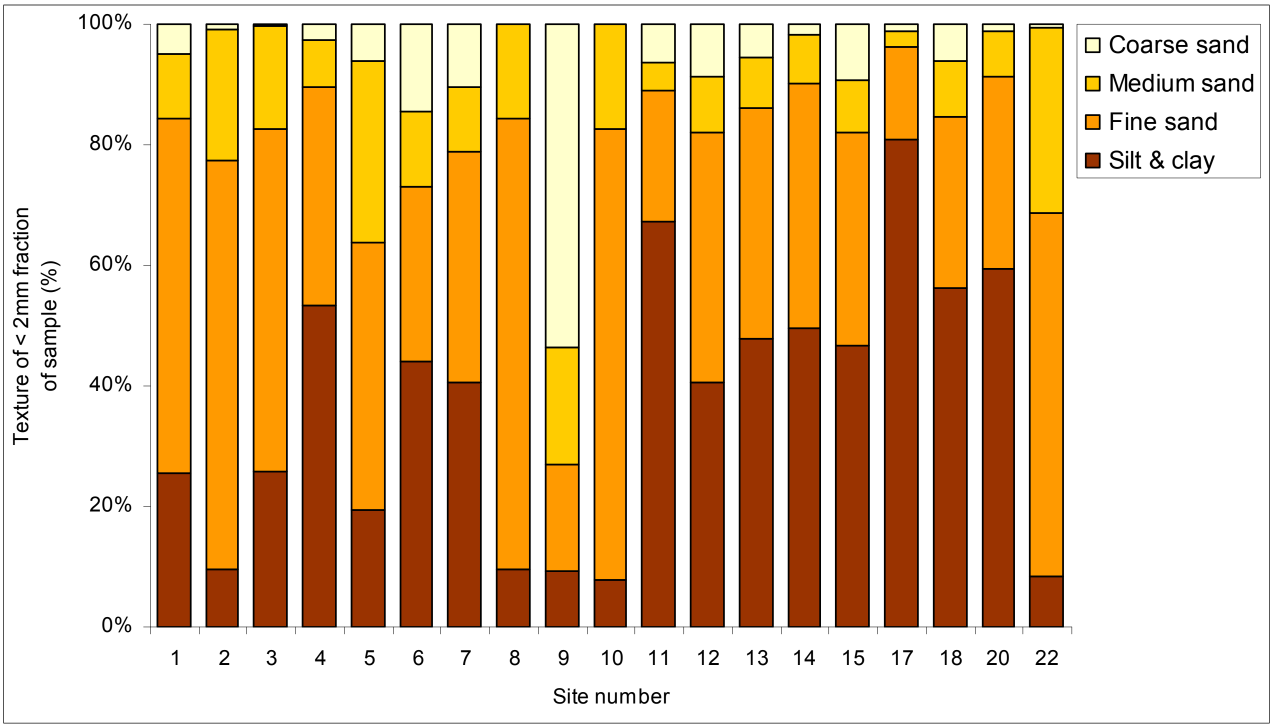


Figure 5: Physical characteristics of the <2 mm fraction of samples

6.0 TRACE ELEMENTS IN WATERWAY SEDIMENTS

6.1 Introduction

Examination of the environmentally significant metals used in our society shows that copper, lead and zinc are the dominant metals (both past and present use) (Sorme et al. 2001).

These elements typically have soil concentrations within urban areas that are on average several times natural concentrations (Linde et al. 2001). Although other elements such as mercury may be present in concentrations that are elevated above the natural concentration, the greatest mass of contaminants usually lies with these three elements (copper, lead and zinc).

This section of the report examines the concentrations of the metals copper, lead and zinc, cadmium, chromium, nickel and also the metalloid element arsenic in sediments from the Styx ICMP area. For the purposes of this report, results for arsenic will be presented alongside the results for metals. All results are compared to land use, soils, data from other locations, sediment quality guidelines and the previous study carried out by Robb (1988).

6.2 Overview of Results

The copper, lead and zinc concentrations in the sediment samples collected from the Styx ICMP area are presented geographically in Figures 6 to 8.

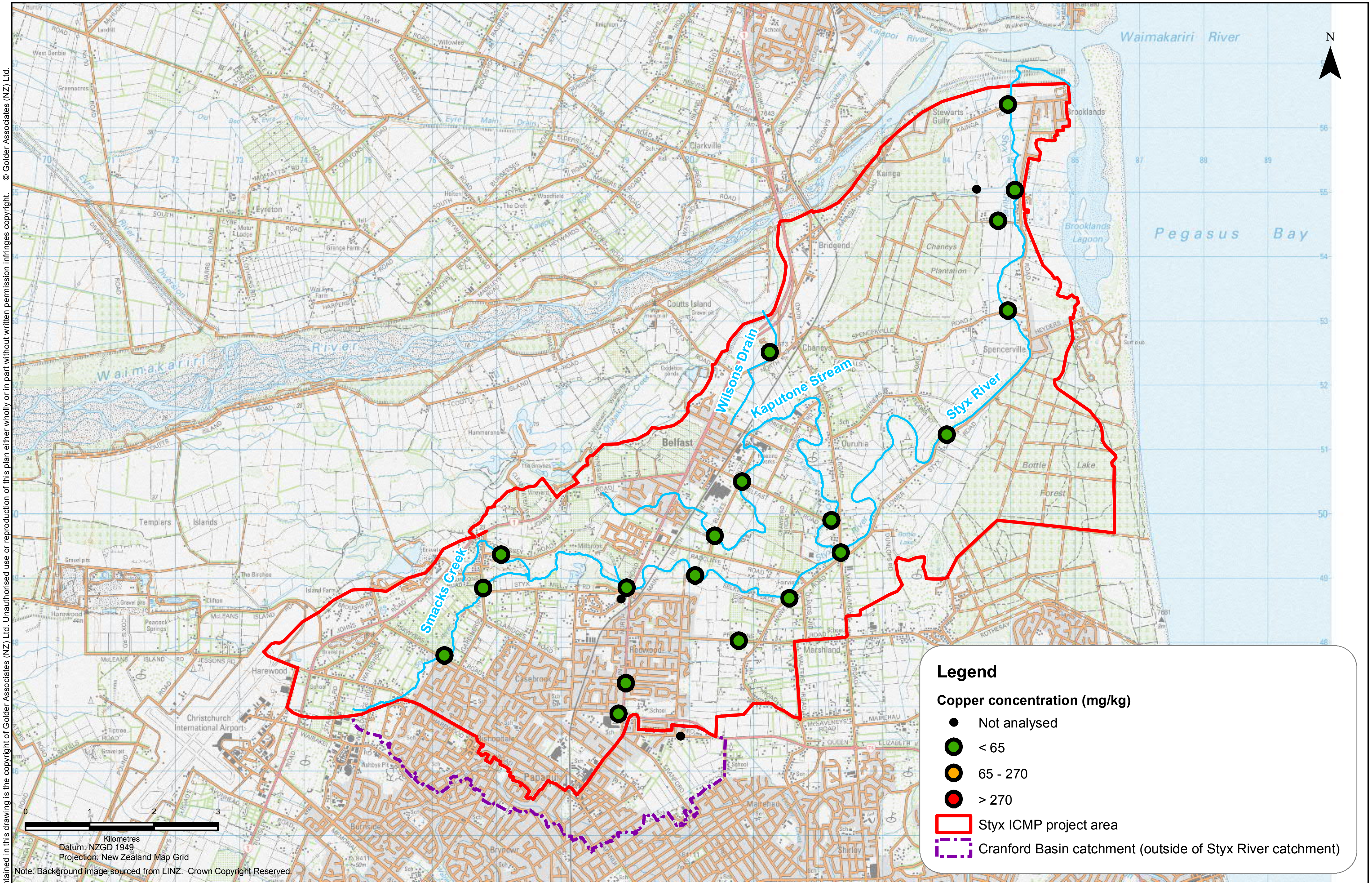
Copper, lead and zinc concentrations demonstrated the greatest variability between sites. Copper concentrations ranged from 3.2 to 45 mg/kg, a factor of 14 difference; lead concentrations ranged from 5.4 to 200 mg/kg, a factor of 40 difference and zinc concentrations ranged from 33 to 760 mg/kg, a factor of 23 difference. In contrast, nickel concentrations for all sites were between 7.7 and 14, a factor of less than 2 difference. Arsenic concentrations ranged from 1.3 to 17 mg/kg and cadmium concentrations were between 0.022 and 0.94 mg/kg.

Lower concentrations of most metals were measured in the mainstem of the Styx River, with typically higher concentrations in the Kaputone Stream and urban drains (Kruses Drain, un-named drain, Horners Drain). The highest concentrations of nickel and zinc and second highest lead concentration from all sediment analysed from within the Styx ICMP area were found in Horners Drain (site 17). The concentration of nickel (20 mg/kg) was double the median concentration of all other samples analysed.

Metal concentrations did not demonstrate any upward or downward increase with distance downstream in the Styx River, although sediments at the most downstream sites (sites 5 and 22) generally had low concentrations of metals, most likely related to the land use of the surrounding area. The sample from the headwaters of the Styx River (site 12) contained elevated lead and zinc concentrations. This may be due to the ephemeral nature of the waterway and the ponding observed at this location: stormwater entering the stream during minor storms may not always be transported downstream and may soak into the stream bed. Stream bed sediments will adsorb and retain metals from the water as it passes through, resulting in elevated metal concentrations in the sediments. This sample, along with that from site 4 in the lower Styx River, also contained the highest proportion of silt and clay of all samples collected from the Styx River.

Lead, and zinc concentrations in the Kaputone Stream (sites 7, 8 and 15) were highly elevated. The concentrations of lead, zinc and also cadmium were the highest in sediments from the most upstream site (site 7), which receives stormwater from a largely urbanised catchment and has in the past received wastewater from meatworks operations in Belfast.

Sediments from Wilsons Drain (site 11) had elevated concentrations of lead and zinc and also a high percentage of mud (71%). The concentrations of arsenic, chromium and nickel were within the upper quartile of all samples analysed from the Styx ICMP area. The drain receives stormwater from the urbanised area of Belfast and discharges to Otukakino Creek, which is not within the Styx River catchment but is within the Styx ICMP area.



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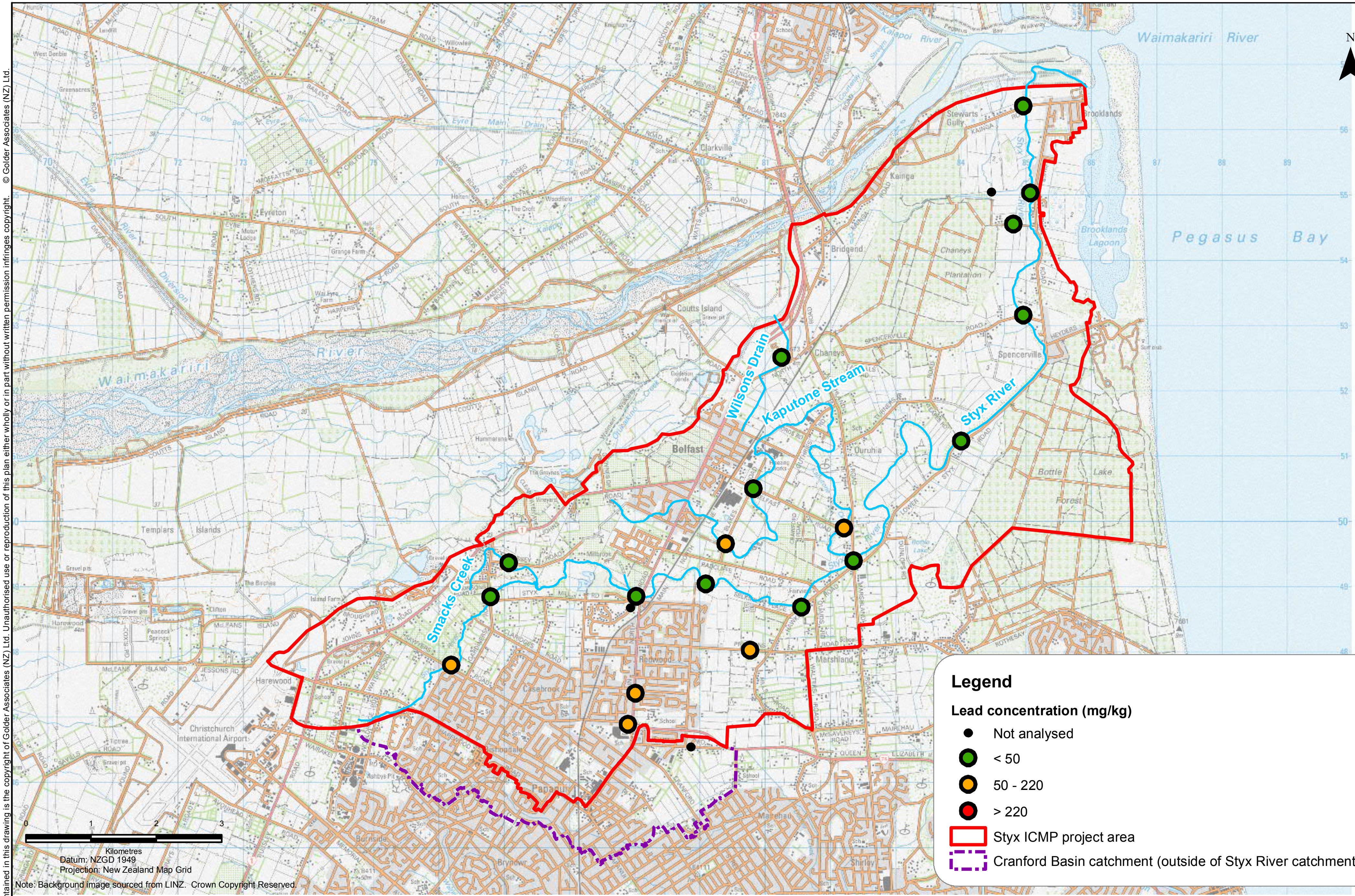

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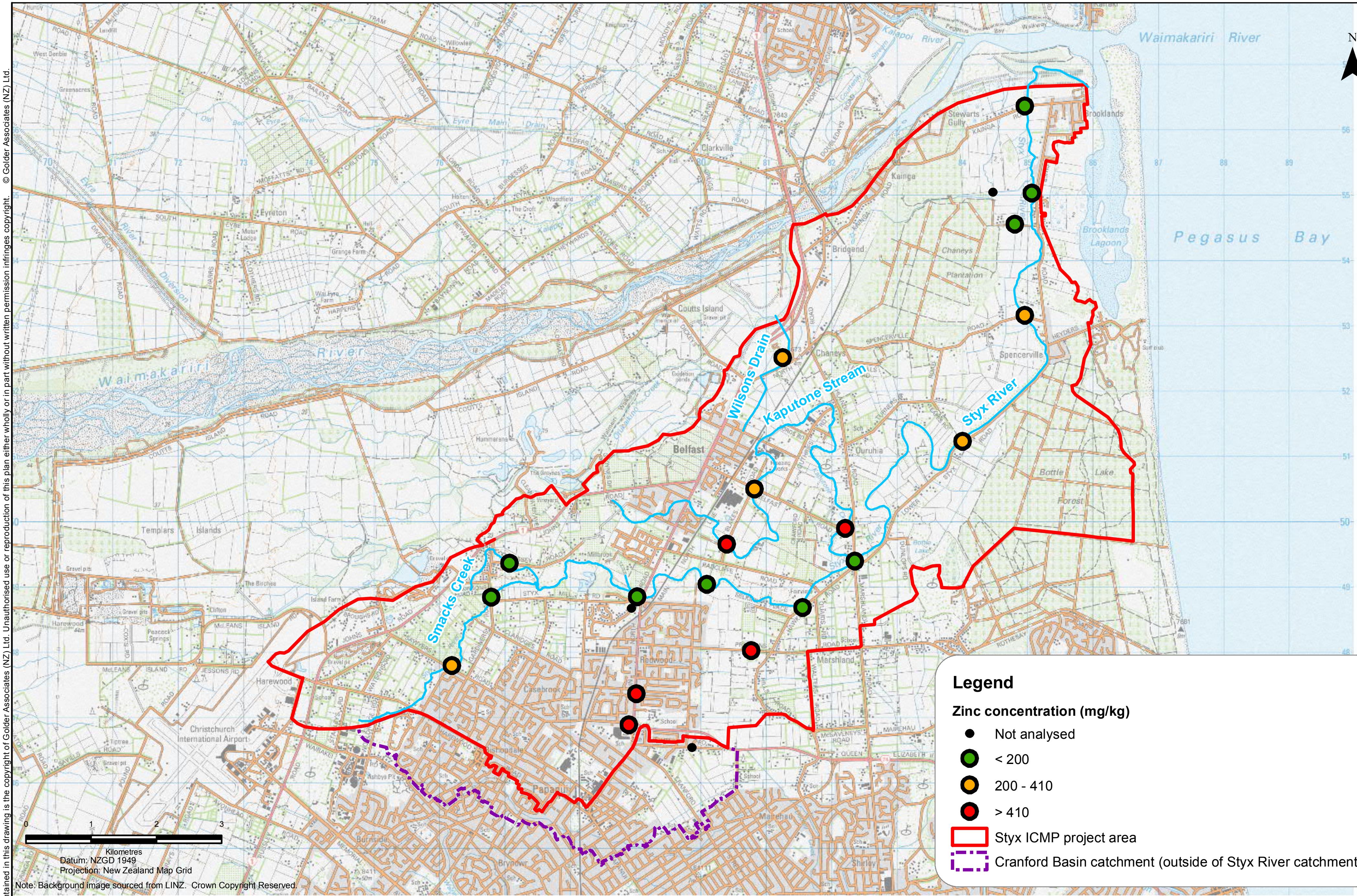

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6.3 Comparison to Soils

The metal concentrations in the sediment samples are listed in Table 7 in comparison to previously reported (Tonkin and Taylor 2007a) soil concentrations for the type surrounding each particular site, based on Environment Canterbury's GIS soil map.

This comparison indicates that cadmium and zinc concentrations were frequently elevated in the sediments compared to soil concentrations. Cadmium concentrations were up to 5 times the previously reported concentration while zinc concentrations were up to 7 times greater. These results suggest enrichment of the sediments with anthropogenic sources of cadmium and zinc. Zinc is a common contaminant in stormwater from road and roof sources, being present in tyres and on metal roofs (e.g., galvanised iron and other roofing products). It is unsurprising that cadmium is also elevated, as, due to common mineralogy, cadmium is often found as an impurity in zinc products, such as in the zinc oxide used in tyres (Kennedy 2003b).

Copper, lead and arsenic concentrations were also elevated over those previously reported for the soil types in the Christchurch area (Tonkin and Taylor 2007a) at several sites. For arsenic and copper, concentrations were typically within the range observed by Tonkin and Taylor (2007a) for soils of a different type, and the elevated results may be partly due to natural variation or misclassification of soil type.

This may also be the case for some of the lead results. The lead concentration in the unnamed drain was double the highest concentration reported by Tonkin and Taylor (2007a) and unlikely to be due to natural variation. Chromium concentrations were elevated in three samples and up to double the concentrations reported by Tonkin and Taylor (2007a). Nickel concentrations were within the range of the previously reported concentrations for the soil types, with four exceptions of a minor increase.

Results above those previously reported by Tonkin and Taylor (2007a) for the Christchurch area provide an indication of potential contamination for a particular site, however the likely higher proportion of fine material (silt and clay) in sediment samples compared to soil samples will also influence the metal concentrations. For samples where all metals are elevated, the sample texture needs to be examined and considered in the interpretation. The influence of sample texture is discussed further in the next section.

Table 7: Trace element concentrations in sediment samples collected from the Styx ICMP area compared to soil concentrations reported by Tonkin and Taylor (2007a).

Waterway	Site	Arsenic	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
Regional recent		**11.5**	**0.18**	**20.8**	**18.8**	**37.4**	**19**	**87**
Styx	1	1.4	0.063	12	8.6	16	9.5	54
Styx	2	1.3	0.088	10	3.5	6.7	7.7	64
Styx	3	2.7	0.067	12	6.4	20	7.8	86
Smacks	6	13	***0.94***	***40***	***31***	20	8.0	76
Kaputone	7	8.8	***0.55***	17	***21***	***72***	11	***610***
Kaputone	8	8.6	***0.35***	***39***	***26***	***52***	10	***430***
Styx	13	6.3	***0.20***	15	13	23	12	***130***
Kaputone	15	9.6	***0.28***	***21***	14	***46***	11	240
Regional gley		**8.7**	**0.24**	**16.8**	**15.5**	**17.8**	**13.4**	**66**
Styx	4	***11***	***0.37***	***30***	***26***	***49***	***14***	***350***
Styx	14	6.6	0.2	***21***	***17***	***27***	12	***230***
Horners	17	***13***	***0.59***	***27***	***45***	***93***	***20***	***760***
Rhodes	18	***15***	0.13	***21***	***16***	***26***	***16***	***87***
Spencerville	20	***14***	0.087	15	9.1	14	12	58

Waterway	Site	Arsenic	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
Regional YBS		**3.4**	**0.06**	**11**	**7.1**	**32**	**8.7**	**51**
Wilsons	11	***14***	***0.28***	***28***	***24***	***48***	***14***	***330***
Styx	22	***4.1***	0.022	11	3.2	5.4	8.6	33
Regional SAGYRE		**6.8**	**0.09**	**13**	**12**	**44**	**19.6**	**47**
Styx	5	3.9	0.052	12	4.4	8.6	9.0	***63***
Urban recent		**15.3**	**0.2**	**19**	**17.7**	**101**	**16.6**	**149**
Styx	12	4.5	**0.25**	15	***29***	74	10	***220***
Urban gley		**10.6**	**0.2**	**18.5**	**23.3**	**35**	**15.6**	**138**
Unnamed	9	***16***	***0.32***	15	***28***	***200***	11	***570***
Kruses	10	***17***	***0.24***	18	23	***53***	11	***700***

Notes: Bold and italicised results indicate values above background soil concentrations. All data mg/kg.

6.4 Influence of Sediment Texture on Metal Concentrations

6.4.1 Introduction

As discussed earlier in this section, the physical characteristics of sediments influence the concentrations of metals (of both natural and anthropogenic origins). The texture of sediments from the Styx ICMP area was described in Section 5.2 and in the following section these are examined together with the concentrations of metals.

6.4.2 Relationship between mud and metals

The particle size of sediments can have a strong influence on metal concentrations, as fine particles have a greater surface area (by weight) than coarse particles, and therefore greater capacity for adsorption of metals. This effect has been examined by plotting metal concentrations against the proportion of mud (silt and clay, <0.063 mm) in samples analysed. Points lying outside the confidence intervals about the line of best fit may be outliers and concentrations are influenced by aspects other than, or additional to, sample texture alone.

Results from this survey are compared to sediment sample data collected in the coastal off-shore environment of Pegasus Bay (data from Kingett Mitchell 2003a, 2003b, 2004b, 2004c). As discussed in Section 3.4, these sediments are comparable due to them having a common natural origin in the Southern Alps, and are consequently referred to as background concentrations in this section.

This comparison (Figure 9) indicates that nickel concentrations are within the range of background concentrations, with all but two samples falling within, or below, the confidence intervals around the line of best fit. Chromium concentrations are also frequently within the background range and indicate a slight increase in concentration with an increasing mud component, though two samples (sites 6 and 8) indicate higher concentrations than would be predicted based on the proportion of mud in the sample, at 40 and 39 mg/kg respectively.

In contrast to these metals, cadmium, lead and zinc concentrations are unmistakeably above the background range, almost irrespective of the mud proportion. For cadmium and zinc, only one sample is found within the predicted range, while seven samples for lead are within the predicted range. These results clearly indicate that the sediments of the Styx ICMP area are not at background concentrations and that there are influences aside from sample texture that are enriching the metal concentrations.

Copper concentrations are also above background concentrations with only two samples within the predicted range. However, copper concentrations in the Styx ICMP area samples tend to be less than three times the maximum observed in off-shore sediments, while cadmium, lead and zinc concentrations were up to 20 times higher than background.

Arsenic concentrations are not influenced by the proportion of mud in samples and are not shown here.

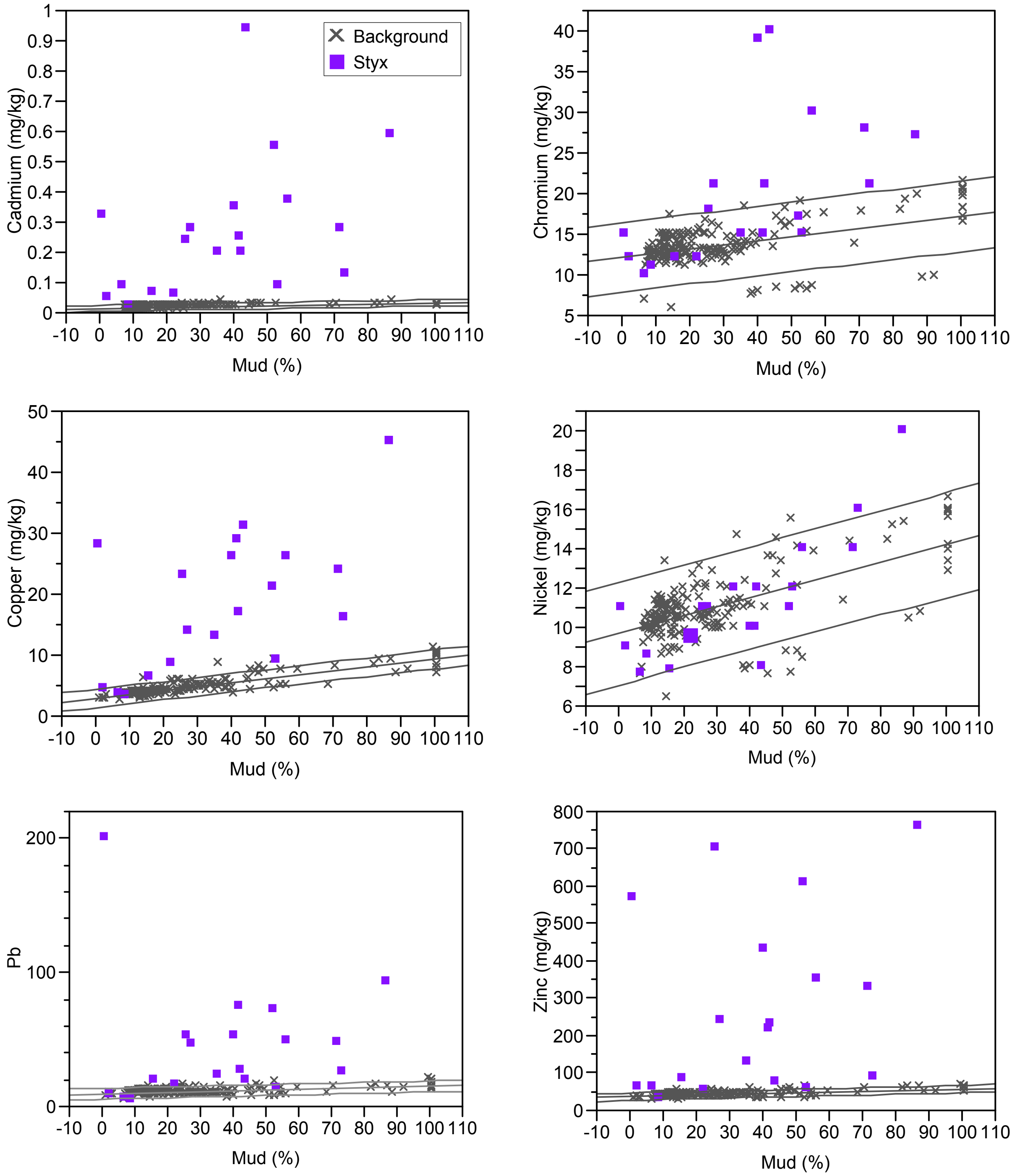


Figure 9: Relationship of metals with mud and comparison to sediments of the same source geology.

6.5 Influence of Land use

6.5.1 Introduction

Land use within the Styx ICMP area ranges from urban to rural as determined by Renard et al. (2004) and shown in Figure 10. The main urban areas are adjacent to Main North Road between Redwood and Belfast. Much of the remaining area is rural and mixed land use. Waterways within the urban areas are typically piped or are boxed drains such as Kruses Drain. Where land use is rural the channels are generally wider and more open, such as the Styx River (site 3), although at this location the land use is described as mixed due to a degree of residential development and a number of intensive horticultural land use areas. The classification of land use areas that have an influence on the sample sites used in this study are shown in Table 8. A conservative approach has been taken for the classification of rural land use sites. For example, parts of Kaputone Stream are within rural areas (site 8), but are classified as mixed land use because of the influence from the urbanised Belfast area upstream.

Table 8: Classification of sites by land use categories.

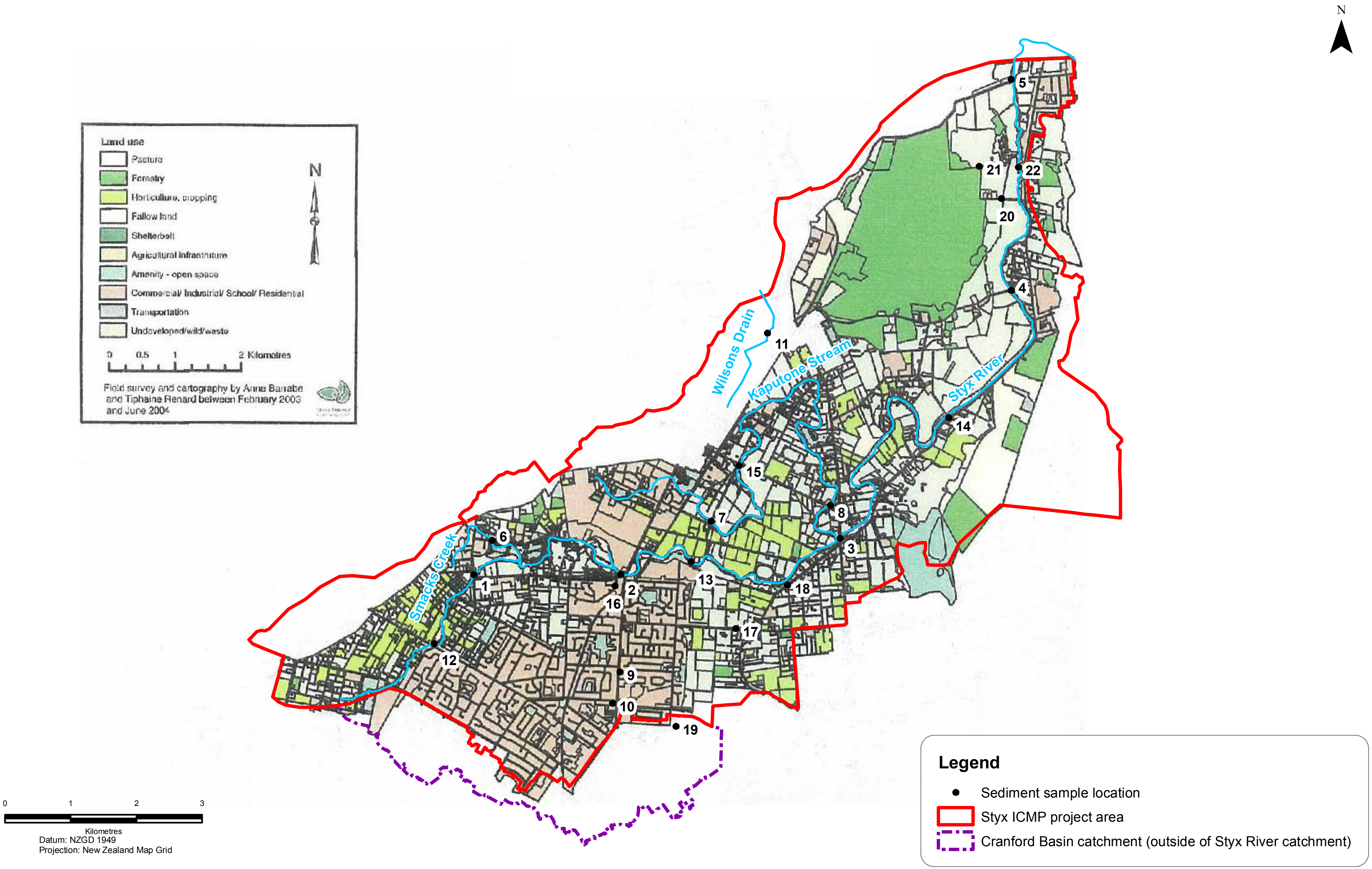
Land use category	Sites included
Urban	6, 7, 9, 10
Rural	18, 20
Mixed (urban and rural)	All others

6.5.2 Differences in metals by land use

As described in Section 2.3, different land uses within a catchment can be expected to generate different contaminant loads that may enter the stream systems. Comparison between sites that have been categorised by their land use (Table 8) was used to determine the extent of the effect the land use has on the sediment quality.

The concentrations of cadmium, copper, lead and zinc were lower in sediments from rural land compared to those from urban land, with all concentrations measured from rural catchment areas less than the overall median concentration and most for urban land greater than the median. Both the highest and lowest concentrations were generally measured in the mixed land use areas of the ICMP area, which are likely to have included both rural and industrial land.

The rural land had higher nickel concentrations than urban land, and were greater than the median concentration of all samples. The highest and the lowest nickel concentrations measured were in the mixed land use parts of the ICMP area where there may have been both rural and urban influences. Chromium concentrations in rural and urban land use areas were similar.



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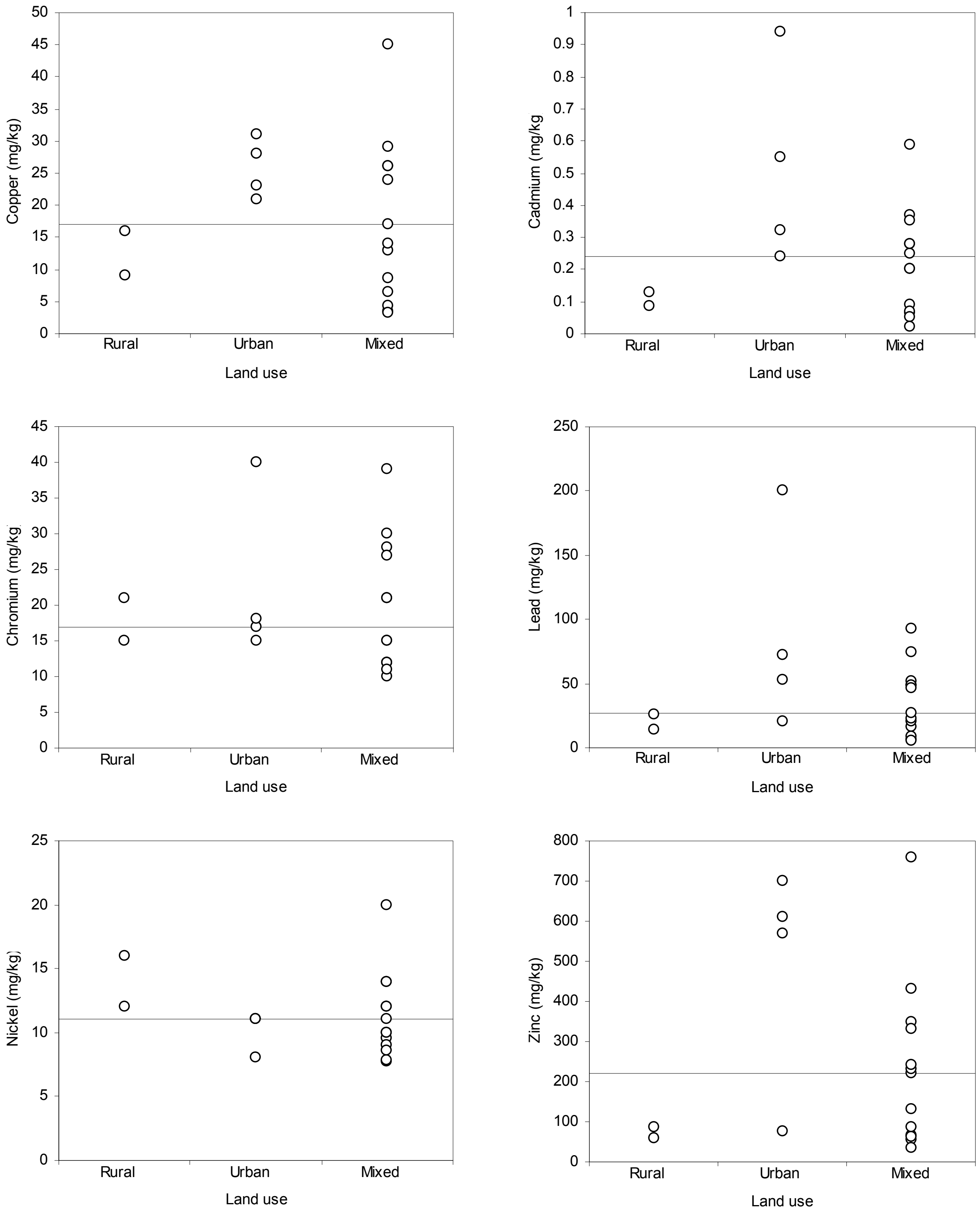


Figure 11: Comparison of metal concentrations in sediments from different land uses. Note: solid line is the overall median.

6.6 Comparison to Other Locations

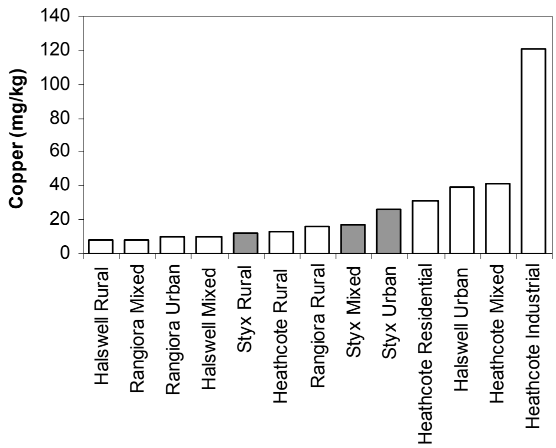
Figure 12 compares the sediments of the Styx ICMP area with sediments from other catchments in Christchurch and Rangiora. Comparative data was acquired from recent studies that used similar or the same analytical methods (Main & Lavender 2003, Kingett Mitchell 2004a, Kingett Mitchell 2005, Golder 2008).

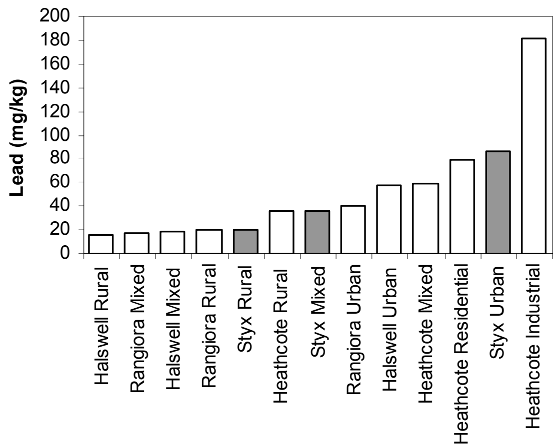
The lowest average concentrations of copper, lead and zinc in the Styx ICMP area were found at the rural sites, while the highest average concentrations of the three metals were found at the urban sites. The rural area of the Halswell River Catchment had the lowest concentrations of copper, lead and zinc of all catchment areas presented in the comparison and sediments from industrial areas within the Heathcote River Catchment had the highest concentrations.

Compared to the other catchments shown in Figure 12, the average concentrations of metals in the rural areas of the Styx ICMP area were generally low. Concentrations of copper, lead and zinc were greater than in sediments from the rural areas within the Halswell catchment. The concentrations of copper and zinc in sediments from rural land use areas in the Styx ICMP area were less than those in rural Rangiora catchments, while copper, lead and zinc were all less than in sediments from Heathcote Rural catchment areas.

Sediments from areas of mixed land use in the Styx ICMP area had copper, lead and zinc concentrations that all were greater than those from mixed land use areas of the Rangiora and Halswell catchments, but less than the Heathcote River Catchment.

The highest concentrations of copper, lead and zinc in sediments from the Styx ICMP area were found in urban areas. The concentrations copper and lead were comparable to urban and residential areas in the Heathcote River Catchment and the average zinc concentration was comparable to urban areas in the Halswell River Catchment.





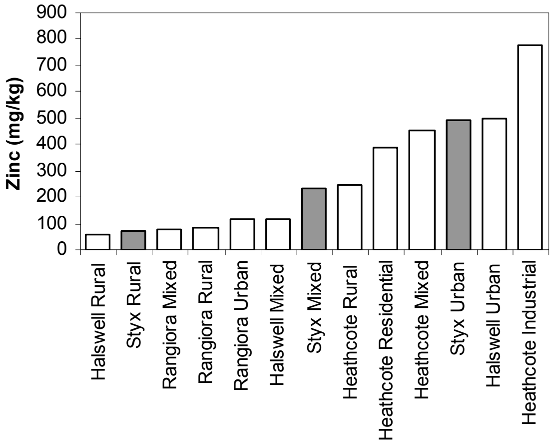


Figure 12: Average concentrations of metals in sediments from catchments in Christchurch and Rangiora.

6.7 Comparison to the 1980 – 1981 Survey

6.7.1 Overview of 1980 Results

Previous sediment quality data for the Styx River Catchment was collected for the Christchurch Drainage Board in 1980 by Robb (1988). The Christchurch Drainage Board measured cadmium, chromium, copper, lead, nickel and zinc in sediments through the Styx River, Kaputone Stream and various rural and stormwater drains (Robb 1988).

The survey results reported by Robb (1988) are presented in Table 9 and indicate seven locations where particularly lead and zinc were measured at elevated concentrations, but generally only one or the other at each site. Kruses Drain was the only location where both lead and zinc were highly elevated. Cadmium was rarely detected in the sediment samples and chromium and nickel were detected at generally low concentrations. The concentration of copper in sediments appeared elevated at a number of sites where either lead or zinc was also elevated (Kruses Drain, Kaputone Stream, Styx River and Rhodes Drain).

Table 9 Metal concentrations in sediments from the Styx River Catchment (Robb 1988)

Waterway	Site No.	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
ANZECC ISQG-low		*1.5*	*80*	*65*	*50*	*21*	*200*
ANZECC ISQG-high		*10*	*370*	*270*	*220*	*52*	*410*
Styx River	2	<0.1	10.5	7.5	20.6	6.7	61.4
Styx River	5	0.1	13.3	27.0	**113**	8.2	140
Styx River	7	<0.1	10.5	3.7	6.6	6.4	36.6
Styx River	10	<0.1	9.6	5.5	13.8	6.0	30.7
Styx River	12	<0.1	5.4	2.9	29	3.4	30.7
Styx River	15	<0.1	10.6	7.5	14	6.6	65.9
Styx River	18	<0.1	6.1	3.9	9.8	4.0	38.2
Styx River	20	0.1	12.0	12.7	21	7.2	129
Styx River	23	<0.1	11.3	5.0	10.8	7.3	59.5
Styx River	26	<0.1	11.2	6.4	13.1	7.3	69.0
Styx River	29	<0.1	15.1	9.5	18.1	9.1	85.6

Waterway	Site No.	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
Styx River	31	<0.1	10.4	3.3	5.3	6.5	28.7
Styx River	33	<0.1	11	6.2	**256**	6.5	69.3
Styx River	35	<0.1	12.5	3.4	8.2	6.9	36.8
Styx River	38	<0.1	12.6	4.3	6.7	7.6	67.0
Styx River	42	<0.1	12.7	4.3	8.2	7.7	41.6
Styx River	47	<0.1	16.1	9.0	11.8	10.4	56.6
Kaputone Stream	K8	<0.1	7.0	5.2	20	4.4	35.5
Kaputone Stream	K15	0.2	15.6	20.2	41	9.5	**366**
Kaputone Stream	K19	<0.1	16.1	29.0	36	7.0	165
Kaputone Stream	K22	<0.1	6.4	3.1	9.0	4.1	72.0
Kaputone Stream	K25	<0.1	6.3	2.4	10.9	3.7	59.0
Kaputone Stream	K28	0.1	14.7	11.5	28	5.8	224
Boundary Drain	Bd2	<0.1	12.3	7.3	19.4	7.5	**1,110**
Canal Reserve Drain	Cr2	<0.1	7.5	8.0	6.3	4.4	29.1
Horners Drain	Ho3	<0.1	12.2	7.6	18.7	9.2	79
Kruses Drain	Kr4	1.4	12.1	29.0	**170.1**	7.0	**744**
Prestons Drain	P1	<0.1	5.8	3.6	21.5	3.3	128
Railway Drain	Rd2	0.1	7.3	8.1	**69**	5.1	93.0
Rhodes Drain	Rh3	0.2	12.7	34.0	**126**	18	125
Shepherds Drain	Sh2	<0.1	15.9	9.5	15.2	10.6	61.4
Spencerville Drain	Sp2	<0.1	9.0	3.6	5.3	5.9	35.8
Styx Drain	Sd1	<0.1	16.7	11.2	18.7	11.6	71.0
Treleavens Drain	Tr4	<0.1	12.1	7.5	10.5	7.4	67.9
Tysons Drain	Ty2	<0.1	17.2	12.0	21.7	11.8	71.3
Winters Road Drain	Wr1	<0.1	8.6	7.2	30.5	5.9	68.5

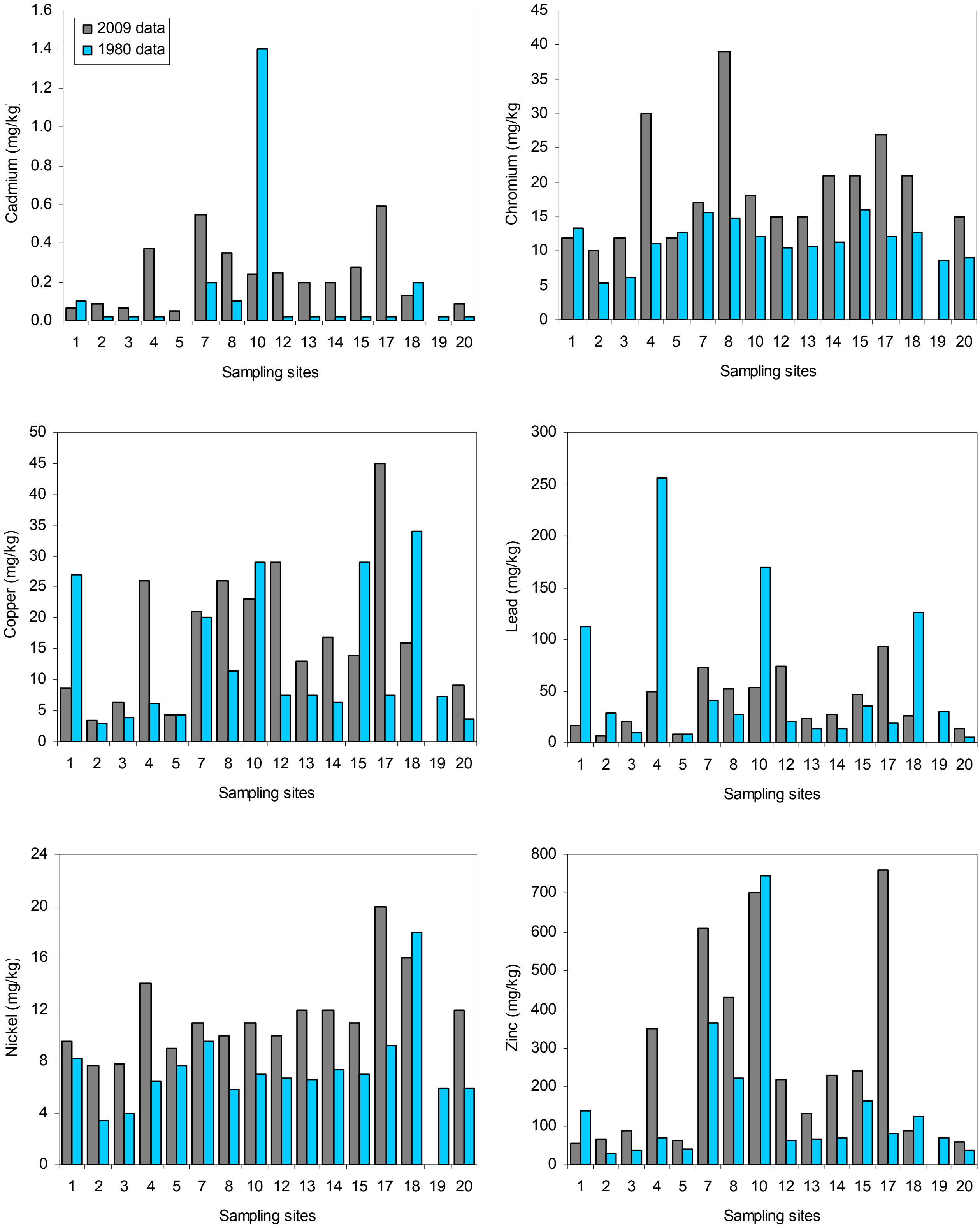
Notes: Bold values exceed ANZECC guidelines. Yellow shading indicates exceedance of ISQG-low, red shading indicates exceedance of ISQG-high. All data mg/kg.

6.7.2 Comparison with Current Survey

Results of the sediment survey undertaken by Robb in 1980-1981 (Robb 1988) are compared to the current results in Figure 13.

Although the chromium concentration in sediments from most sites appear to have changed little over time, there were reasonable increases at sites 4, 8 and 17.

Nickel concentrations appear to have increased slightly overall since the 1980/81 survey, but as discussed in Section 6.4.2, the concentration of nickel in sediments from all except four sites sampled in 2009 were within the confidence intervals that were used to determine a background level. Cadmium was generally below the detection limit in the 1980/81 survey, but was measured at higher concentrations in 2009. The cadmium concentration decreased from 1.4 to 0.24 mg/kg in sediment from Kruses Drain (site 10) between the two studies. Copper concentrations in increased the most in the Styx River sediments at the headwaters (site 12) and at downstream sites 20, 4 and 14. The concentration of lead increased by more than 50% at five sites and decreased by more than 50% at five sites, and similarly to copper, these changes occurred at sites near the headwaters or the downstream sections of the Styx River, while the concentrations of lead in sediments in the area around Belfast (sites 7,13 and 15) generally changed by less than 50%.



Note: Cadmium data from Robb (1988) below detection limit of 0.05 mg/kg is plotted at half detection limit.

Figure 13: Comparison of metal and metalloid concentrations in 2009 (this study) and 1980/81 (Robb 1988).

The number of relative changes to metal concentrations and the mud composition is presented in Figure 14 and shows that from the increase in zinc concentrations in sediments at 12 out of 16 sites shown in Figure 13, six of these were increases by more than 50% compared to just one decrease by the same extent. While cadmium concentrations were greater than in 1980 at twelve of the fifteen sites, lead concentrations were at least 50 % lower at five sites. Chromium and nickel concentrations varied the least, with changes of at least 50 % at twelve and eleven sites respectively. Just two sites had a change in mud content of more than 50%, which indicates that a change in sample texture was not likely to have been responsible for the changes in metal concentrations.

6.8 Implications of Changes in Metal Concentrations in Sediments

6.8.1 Introduction

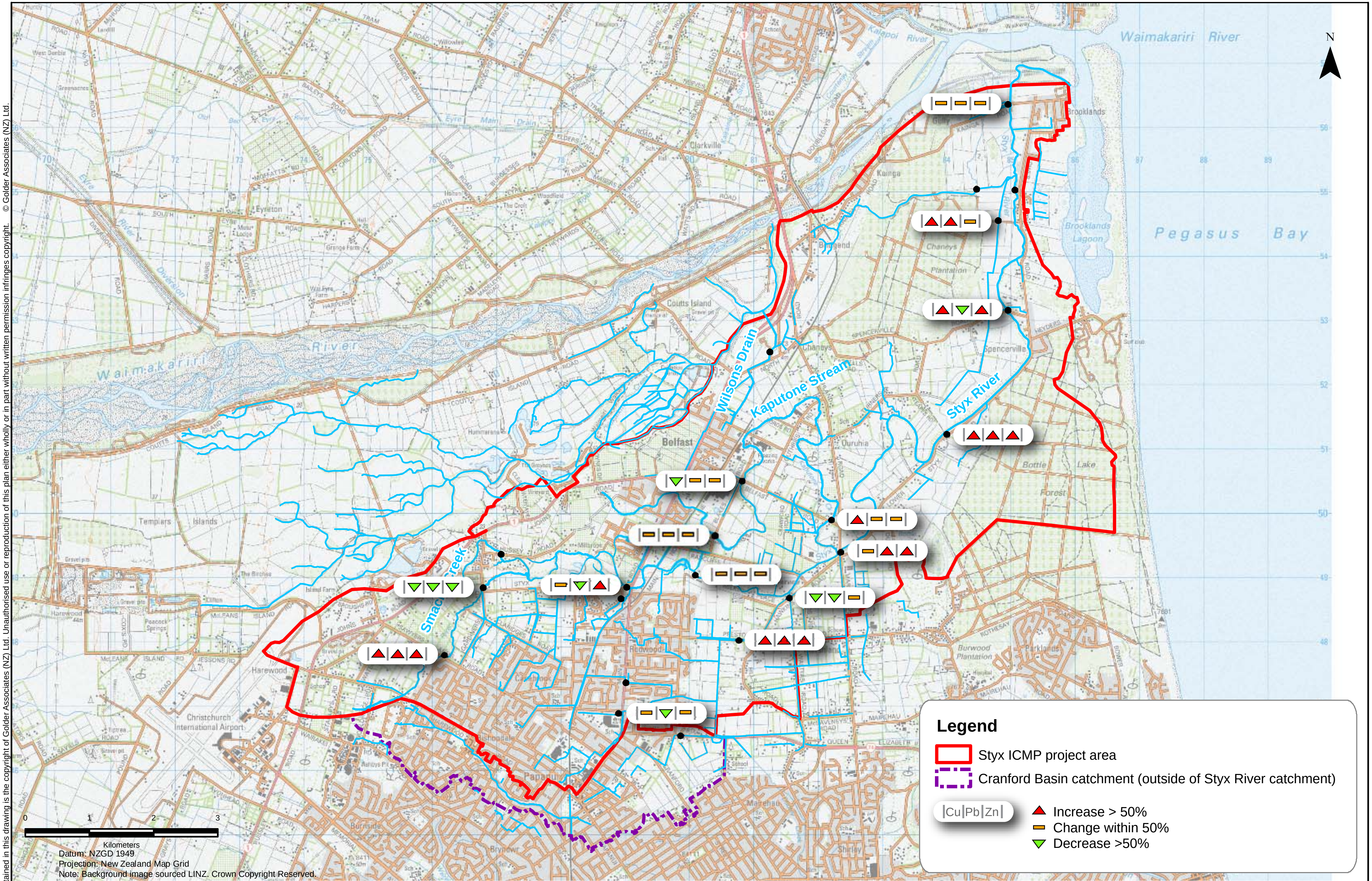
The ANZECC (2000) sediment quality guidelines (Table 3) are used in this section to assess the potential effects that sediment quality may have on biological communities inhabiting the stream. Increased concentrations of metals in stream sediments have the potential to adversely affect stream biota that inhabit these sediments. Toxicity arises through the exposure of organisms to pore water within the sediments. Metals adsorbed to sediment particles are in equilibrium with the metals in the pore water. The concentration in the pore water is a function of many factors including the redox state of the sediment (how much oxygen is present) and the rate of diffusion between the pore water and the overlying stream waters. Concentrations can in some situations become high enough to exert toxic effects on biota. It should be noted however, that toxicity may arise from constituents other than metals. Ammoniacal nitrogen is common in stream-bed sediments especially if organic matter builds up and the sediments become anaerobic. A number of studies have shown that ammoniacal nitrogen in sediments is often implicated as the prime causal agent of toxicity. Elevated concentrations of contaminants in stream water and in stream sediment is also likely to result in increased elemental concentrations in biofilms within stream systems. These biofilms, which include coatings of bacteria and fungi and other organisms (periphyton) on hard substrates and plants within streams, can contain significantly elevated concentrations of metals (many times higher than stream sediments). These high concentrations occur because the combination of organic matter and chemical precipitates in the coatings tend to have an affinity for trace metals. Because these biofilms are utilised as a food source by grazing organisms within stream systems, associated contaminants can be transferred to other organisms within the stream food web.

6.8.2 Comparison to guidelines

The metal concentrations in the sediment samples from the Styx ICMP area are listed and compared to the ANZECC (2000) sediment quality guidelines in Table 10. Lead and zinc were the only metals to exceed the ANZECC (2000) guidelines. Six samples exceeded the lead ISQG-low of 50 mg/kg, but no sample exceeded the lead ISQG-high. Ten samples exceeded the zinc ISQG-low of 200 mg/kg, with five of these also exceeding the zinc ISQG-high of 410 mg/kg.

Only a third of the nine samples from the Styx River mainstem exceeded any of the ANZECC (2000) guidelines, while all three samples from the Kaputone Stream exceeded zinc guidelines and two exceeded the lead guidelines. Zinc concentrations exceeded the ISQG-high at two out of the three sites in the Kaputone Stream.

Adverse effects on biota can be expected to occasionally occur when metal concentrations are above the ISQG-low but below the ISQG-high, whereas adverse effects in biota are expected to frequently occur when the ISQG-high is exceeded. This suggests the potential for effects on the instream biota within the Styx River at sites 12, 14 and 4 and in Wilsons Drain, and the likelihood of adverse effects in Kaputone Stream, Kruses Drain, Horners Drain and the unnamed drain. It should be noted that although concentrations may be higher than the guidelines, toxicity is still very dependent on the form of the element in the sediment (as some forms are relatively stable geochemically). Increased stability is likely to reduce toxicity.



Golder Associates

TITLE COMPARISON OF METAL CONCENTRATIONS FROM 2009 AND 1980/81 (ROBB 1988) SAMPLES.

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Table 10: Trace element concentrations in sediment samples collected from the Styx River Catchment.

Waterway	Site	Arsenic	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
ANZECC ISQG-low		***20***	***1.5***	***80***	***65***	***50***	***21***	***200***
ANZECC ISQG-high		***70***	***10***	***370***	***270***	***220***	***52***	***410***
Styx	12	4.5	0.25	15	29	**74**	10	**220**
Styx	1	1.4	0.063	12	8.6	16	9.5	54
Styx	2	1.3	0.088	10	3.5	6.7	7.7	64
Styx	13	6.3	0.20	15	13	23	12	130
Styx	3	2.7	0.067	12	6.4	20	7.8	86
Styx	14	6.6	0.2	21	17	27	12	**230**
Styx	4	11	0.37	30	26	49	14	**350**
Styx	22	4.1	0.022	11	3.2	5.4	8.6	33
Styx	5	3.9	0.052	12	4.4	8.6	9.0	63
Smacks	6	13	0.94	40	31	20	8.0	76
Kaputone	7	8.8	0.55	17	21	**72**	11	**610**
Kaputone	15	9.6	0.28	21	14	46	11	**240**
Kaputone	8	8.6	0.35	39	26	**52**	10	**430**
Unnamed	9	16	0.32	15	28	**200**	11	**570**
Kruses	10	17	0.24	18	23	**53**	11	**700**
Wilsons	11	14	0.28	28	24	48	14	**330**
Horners	17	13	0.59	27	45	**93**	20	**760**
Rhodes	18	15	0.13	21	16	26	16	87
Spencerville	20	14	0.087	15	9.1	14	12	58

Notes: Bold values exceed ANZECC guidelines. Yellow shading indicates exceedance of ISQG-low, red shading indicates exceedance of ISQG-high. All data mg/kg.

6.8.3 Comparison to previous survey

The results of Robb (1988) indicated generally low exceedance of ANZECC (2000) sediment quality guidelines. Seven of the 36 samples collected in 1981 by Robb exceeded the guidelines for either lead or zinc (see Section 3.2 for full results). Of the six locations reanalysed in 2009, four continued to exceed ISQG-low guidelines for either lead or zinc (Table 11). Furthermore, there was a greater exceedance of the ISQG-high for zinc in 2009. In contrast, at three locations, lead concentrations, which had been above the ISQG-low (sites 1 and 18) or high (site 4) were lower in 2009 and below the guidelines. At site 4 in the Styx River, zinc concentrations were previously below the ISQG-low, but in 2009 exceeded this guideline.

Table 11: Comparison of lead and zinc concentrations to Robb (1988).

Waterway	Site No.		Lead		Zinc	
	1980/1981	2009	1980/1981	2009	1980/1981	2009
ANZECC ISQG-low			*50*		*200*	
ANZECC ISQG-high			*220*		*410*	
Styx River	5	1	**113**	16	140	54
Styx River	33	4	**256**	49	69	**350**
Kaputone Stream	K15	7	41	**72**	**366**	**610**
Kaputone Stream	K28	8	28	**52**	**224**	**430**
Kruses Drain	Kr4	10	**170**	**53**	**744**	**700**
Rhodes Drain	Rh3	18	**126**	26	125	87

Notes: Bold values exceed ANZECC guidelines. Yellow shading indicates exceedance of ISQG-low, red shading indicates exceedance of ISQG-high. All data mg/kg.

7.0 POLYCYCLIC AROMATIC HYDROCARBONS

7.1 Introduction

PAHs are ubiquitous within urban environments. The literature on the distribution of PAHs in air, water, soils and sediments in and near urban environments is extensive. PAHs are a relatively complex group of aromatic compounds. Typically, environmental evaluations examine a limited number of key compounds based around the list of USEPA priority pollutants developed a number of years ago.

PAHs are derived from many sources. These sources are often classified as petrogenic (derived from petroleum) or pyrogenic (derived from combustion processes including the use of fuels). The relative sources of PAH in any given urban area are site specific. As such, many studies show different source apportionment between vehicle emissions, combustion of coal and coke and other sources. For example, Simcik et al. (1999) estimated that around Chicago, coal combustion accounted for 48% of PAHs in the atmosphere, natural gas combustion 26%, coke ovens 14% and vehicle emissions 9%. Dickhut et al. (2000) examined contributions to Chesapeake Bay and found that motor vehicles were the most significant source of some PAHs (e.g., benzo[a]pyrene). 53% of the PAHs in the sea-surface microlayer near urban areas was identified as derived from motor vehicle emissions and 47% coal derived. When the sediments were examined 86% of PAHswere coal derived and 14% vehicle derived.

PAHs are present in urban runoff and in the runoff from motorways and roads. PAH concentrations in road surface dusts in New Zealand have been reported to be around 1.46 mg/kg (Waitakere City – Kennedy & Gadd 2003). A number of studies in New Zealand have reported PAH data for urban stormwater (e.g., Sherriff 1998, Brown et al. 2003, O'Reilly et al. 2002 and Timperley et al. 2003).

7.2 Survey Results

PAHs were measured above the detection limit of analysis in eight of the eighteen samples analysed from the Styx River, Kaputone Stream and urban and rural drains. None of the seventeen PAH compounds assessed were detected in the remaining ten samples. The highest concentrations of PAHs were measured in the sample from Wilsons Drain, at a location within the Otukaikino Memorial Reserve.

The most frequently detected compounds were fluoranthene, pyrene, phenanthrene, benzo[b]fluoranthene and benzo[j]fluoranthene. These compounds were each detected in all eight samples and were typically the compounds measured at the highest concentrations. The compounds fluoranthene, pyrene and phenanthrene are associated with combustion of fossil fuels.

Some of the lighter PAH compounds were less frequently detected. Naphthalene was not detected in any sediment samples, and both fluorene and acenaphthene were detected only in the sample from Wilsons Drain.

Table 12: PAHs concentrations in sediment samples collected from the Styx River (in order of upstream to downstream).

	ANZECC Guidelines		Sawyers Arms	Gardiners	Main North	Redwood	Marshlands	Teapes	Spencerville	Brooklands	Floodgates
	ISQG-Low	ISQG-High	12	1	2	13	3	14	4	22	5
Acenaphthene	0.016	0.5	<0.065	<0.038	<0.034	<0.060	<0.035	<0.052	<0.12	<0.037	<0.053
Acenaphthylene	0.044	0.64	<0.065	<0.038	<0.034	<0.060	**0.050**	<0.052	<0.12	<0.037	<0.053
Anthracene	0.085	1.1	<0.065	<0.038	<0.034	<0.060	**0.092**	<0.052	<0.12	<0.037	<0.053
Benzo[a]anthracene	0.261	1.6	**0.073**	<0.038	<0.034	<0.060	**0.33**	**0.053**	<0.12	<0.037	<0.053
Benzo[a]pyrene (BAP)	0.43	1.6	<0.065	<0.038	<0.034	<0.060	**0.41**	<0.052	<0.12	<0.037	<0.053
Benzo[b]fluoranthene + Benzo[j]fluoranthene			**0.084**	<0.038	<0.034	<0.060	**0.48**	**0.11**	<0.12	<0.037	<0.053
Benzo[g,h,i]perylene			<0.065	<0.038	<0.034	<0.060	**0.28**	<0.052	<0.12	<0.037	<0.053
Benzo[k]fluoranthene			<0.065	<0.038	<0.034	<0.060	**0.21**	<0.052	<0.12	<0.037	<0.053
Chrysene	0.384	2.8	**0.084**	<0.038	<0.034	<0.060	**0.35**	**0.052**	<0.12	<0.037	<0.053
Dibenzo[a,h]anthracene	0.063	0.26	<0.065	<0.038	<0.034	<0.060	**0.045**	<0.052	<0.12	<0.037	<0.053
Fluoranthene	0.6	5.1	**0.26**	<0.038	<0.034	<0.060	**0.82**	**0.086**	<0.12	<0.037	<0.053
Fluorene	0.019	0.54	<0.065	<0.038	<0.034	<0.060	<0.035	< 0.052	<0.12	<0.037	<0.053
Indeno(1,2,3-c,d)pyrene			<0.065	<0.038	<0.034	<0.060	**0.17**	< 0.052	<0.12	< 0.037	<0.053
Naphthalene	0.16	2.1	<0.33	<0.19	<0.17	<0.30	<0.18	<0.26	<0.56	<0.19	<0.27
Phenanthrene	0.24	1.5	**0.17**	<0.038	< 0.034	<0.060	**0.37**	**0.068**	<0.12	<0.037	<0.053
Pyrene	0.665	2.6	**0.26**	<0.038	<0.034	<0.060	**0.88**	**0.099**	<0.12	<0.037	<0.053
Total PAHs [1]	4.0	45.0	**1.39**	ND [2]	ND	ND	**4.61**	<0.052	ND	ND	ND

Notes: Values in bold are above detection limit. [1] Sum of all 17 PAHs measured (half of detection limit used for compounds that are below detection). [2] None detected, total PAHs not calculated. All data mg/kg.

Table 13: PAHs concentrations in sediment samples collected from tributaries and drains of the Styx River.

	Smacks Creek	Kaputone Stream	Kaputone Stream	Unnamed Drain	Kruses Drain	Horners Drain	Wilsons Drain	Rhodes Drain	Spencerville Drain
	6	7	8	9	10	17	11	18	20
Acenaphthene	<0.18	<0.11	<0.12	<0.031	<0.042	<0.072	**0.18**	<0.056	<0.065
Acenaphthylene	<0.18	<0.11	<0.12	**0.041**	**0.044**	<0.072	**0.1**	<0.056	<0.065
Anthracene	<0.18	<0.11	<0.12	**0.053**	<0.042	<0.072	**0.58**	<0.056	<0.065
Benzo[a]anthracene	<0.18	<0.11	<0.12	**0.19**	**0.087**	**0.31**	**0.75**	<0.056	<0.065
Benzo[a]pyrene (BAP)	<0.18	<0.11	<0.12	**0.25**	**0.20**	**0.37**	**0.81**	<0.056	<0.065
Benzo[b]fluoranthene + Benzo[j]fluoranthene	<0.18	**0.11**	<0.12	**0.26**	**0.24**	**0.74**	**0.86**	<0.056	<0.065
Benzo[g,h,i]perylene	<0.18	<0.11	<0.12	**0.22**	**0.18**	**0.26**	**0.38**	<0.056	<0.065
Benzo[k]fluoranthene	<0.18	<0.11	<0.12	**0.18**	**0.13**	**0.24**	**0.49**	<0.056	<0.065
Chrysene	<0.18	<0.11	<0.12	**0.24**	**0.14**	**0.32**	**0.85**	<0.056	<0.065
Dibenzo[a,h]anthracene	<0.18	<0.11	<0.12	**0.032**	<0.042	<0.072	**0.085**	<0.056	<0.065
Fluoranthene	<0.18	**0.17**	<0.12	**0.44**	**0.31**	**0.6**	**2.5**	<0.056	<0.065
Fluorene	<0.18	<0.11	<0.12	<0.031	<0.042	<0.072	**0.51**	<0.056	<0.065
Indeno(1,2,3-c,d)pyrene	<0.18	<0.11	<0.12	**0.12**	**0.11**	**0.19**	**0.26**	<0.056	<0.065
Naphthalene	<0.90	<0.52	<0.60	<0.16	<0.21	<0.36	<0.39	<0.28	<0.33
Phenanthrene	<0.18	**0.11**	<0.12	**0.23**	**0.29**	**0.52**	**3.3**	<0.056	<0.065
Pyrene	<0.18	**0.18**	<0.12	**0.50**	**0.32**	**0.67**	**2.4**	<0.056	<0.065
Total [1]	ND[2]	**1.49**	ND	**2.87**	**2.24**	<0.072	**14.3**	<0.056	<0.065

Notes: Values in bold are above detection limit. [1] Sum of all 17 PAHs measured (half of detection limit used for compounds that are below detection). [2] None detected, total PAHs not calculated. All data mg/kg.

7.3 Influence of Organic Carbon and Sediment Texture

The concentration of organic carbon in a sediment sample affects the concentrations of organic contaminants as these compounds readily adsorb to organic carbon. Sediments that contain high concentrations of organic carbon are therefore more likely to accumulate greater concentrations of organic contaminants (including PAHs) if present and available in the waterway.

Total organic carbon concentrations were extremely variable in the sediment samples, with highest concentrations measured in samples from Smacks Creek (site 6) and Kaputone Stream (sites 7 & 8). These three samples did not contain elevated PAHs. PAHs were not detected in the samples from sites 6 and 8 and only four compounds (of a possible 16) were detected in the sample from site 7.

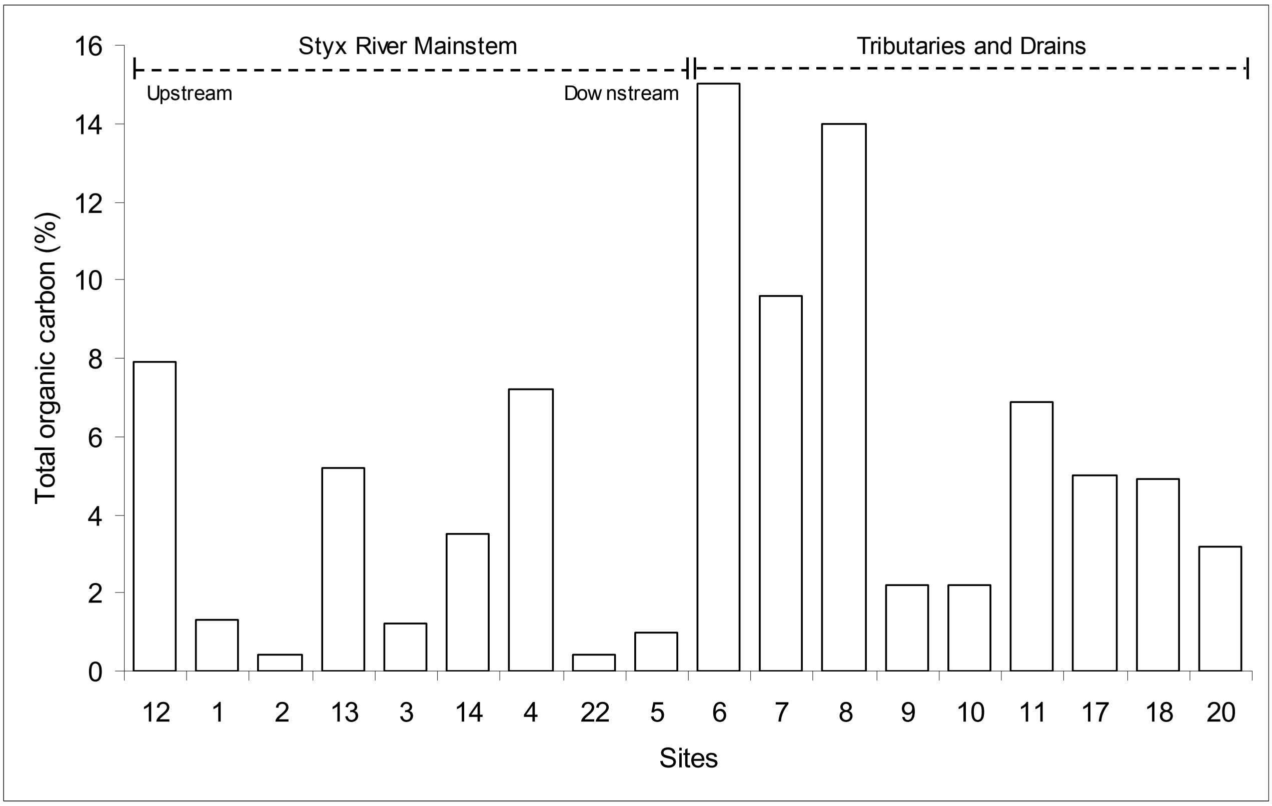

Figure 15: Total organic carbon content (%) in sediment samples from the Styx River Catchment.

The total organic carbon content is compared to total PAH concentrations for the sediment samples that contained detectable concentrations of PAHs in Figure 16. This comparison does not suggest any relationship between these parameters, however it is very limited due to the small data set (as few samples contained PAHs above the screening detection limits). Previously Kingett Mitchell (2005) reported a general relationship between total organic carbon content and total PAHs, for samples from the Heathcote and Halswell River catchments that contained less than 5 mg/kg of total PAHs.

Similarly, there was no apparent relationship between the proportion of mud in the samples and the concentration of total PAHs. As with the current study, there was no relationship between the percentage of mud (silt & clay particles) and total PAHs in samples collected from the Heathcote and Halswell River catchments (Kingett Mitchell 2005).

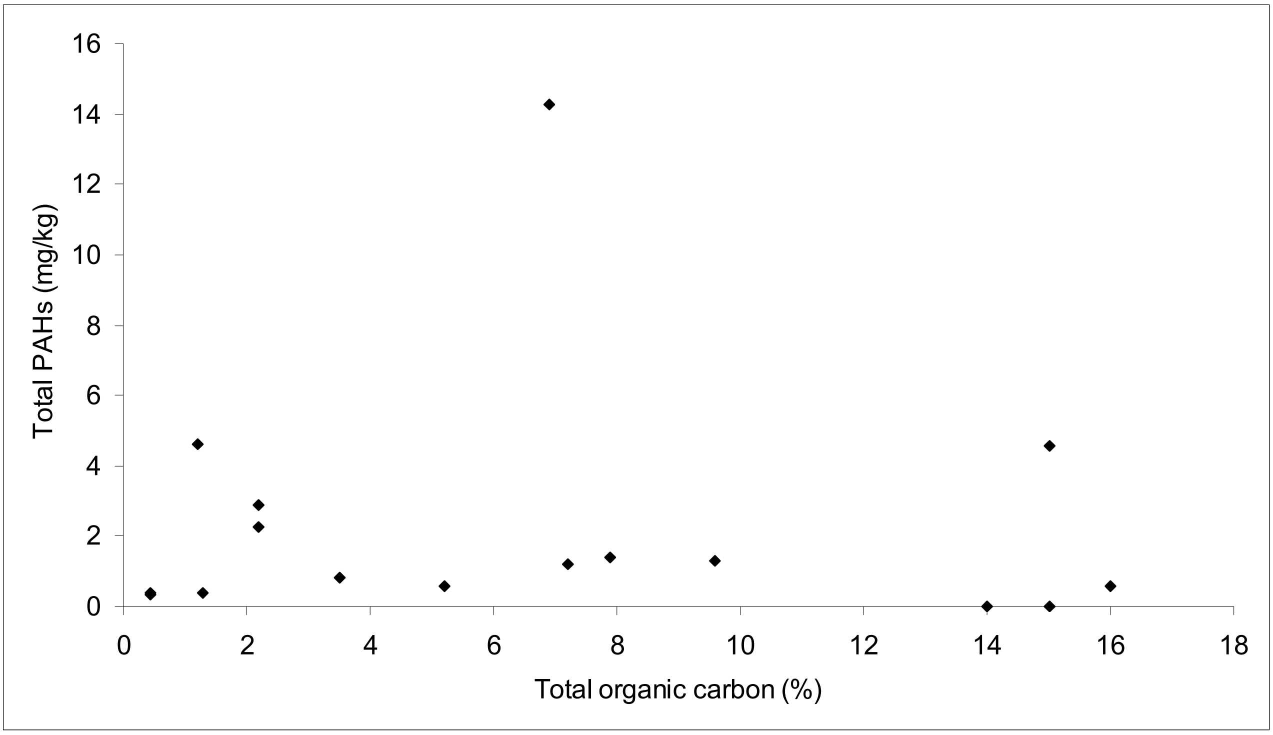

Figure 16: Relationship between total organic carbon and total PAHs in sediment samples.

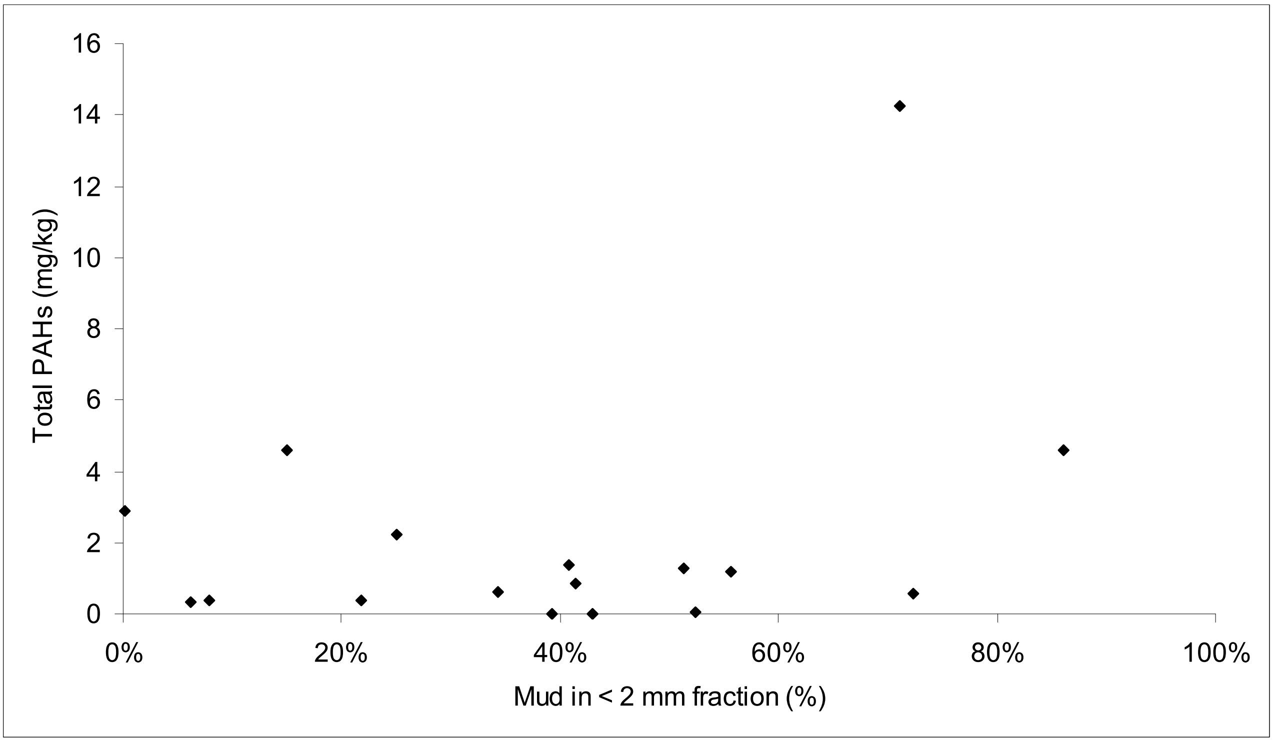

Figure 17: Relationship between mud fraction and total PAHs in sediment samples.

7.4 Comparison to Other Locations

The maximum total PAHs concentration measured in this study was 14.3 mg/kg in the sample from Wilsons Drain (site 11), which receives stormwater from the northern motorway. Concentrations were substantially higher than in sediments from Curletts Drain, adjacent to the Christchurch Southern Motorway (total of 1.5 mg/kg, Kingett Mitchell 2005). The total PAH concentration at this location was also well above the median of 2.6 mg/kg for the same compounds in sediment samples from the Heathcote River catchment (Kingett Mitchell 2005). The maximum detected in that study was 45.2 mg/kg, in a sample from the Heathcote River downstream of the confluence with Cashmere Stream.

Sediments from the lower reaches of the Styx River had low concentrations and all compounds were below detection at the three most downstream locations. The maximum concentrations at these sites, based on the detection limits for each sample, are similar to, or lower than those measured in the Halswell River (total PAHs 0.09 to 0.65 mg/kg, Kingett Mitchell 2005). The detection limit used in that study was somewhat lower than that used in the current study.

The sediments from Rhodes Drain and Winters Road Drain, both located within a rural catchment area, had low PAH concentrations and all compounds measured were below the level of detection. Based on the detection limits, the total PAH concentrations of the same compounds were less than those measured in the rural catchment of the Heathcote River (PAHs 0.09 – 2.8 mg/kg, Kingett Mitchell 2005), but similar or lower than the Halswell River (0.21 – 0.59 mg/kg, Kingett Mitchell 2005). This was due to the higher limit of detection in the current study.

7.5 PAH and Land use

The effects of land use on the PAH concentrations were investigated by categorising the sites according to land use as discussed in Section 6.5. The data shown in Figure 18 has been normalised to total organic carbon content (i.e., the PAHs present based upon 1% TOC).

The main sources of PAHs in the Christchurch area are from pyrogenic sources, specifically from the combustion of wood and from vehicle emissions (Tonkin and Taylor 2007b). Therefore, the sediments that had the highest PAH concentrations in the Styx ICMP area could be expected where runoff is from areas with combustion (residential or industrial heating).

Figure 18 indicates that the concentrations of PAHs in the Styx ICMP area were low in sediments from rural sites compared to the sediments from urban or mixed land sites that had elevated concentrations. The mixed sites had the highest apparent concentrations of total PAHs, with the highest concentrations found at site 3 in the Styx River and in Wilsons Drain (site 11) where the sediments contained individual PAHs that exceeded the ANZECC ISQG-low guidelines.

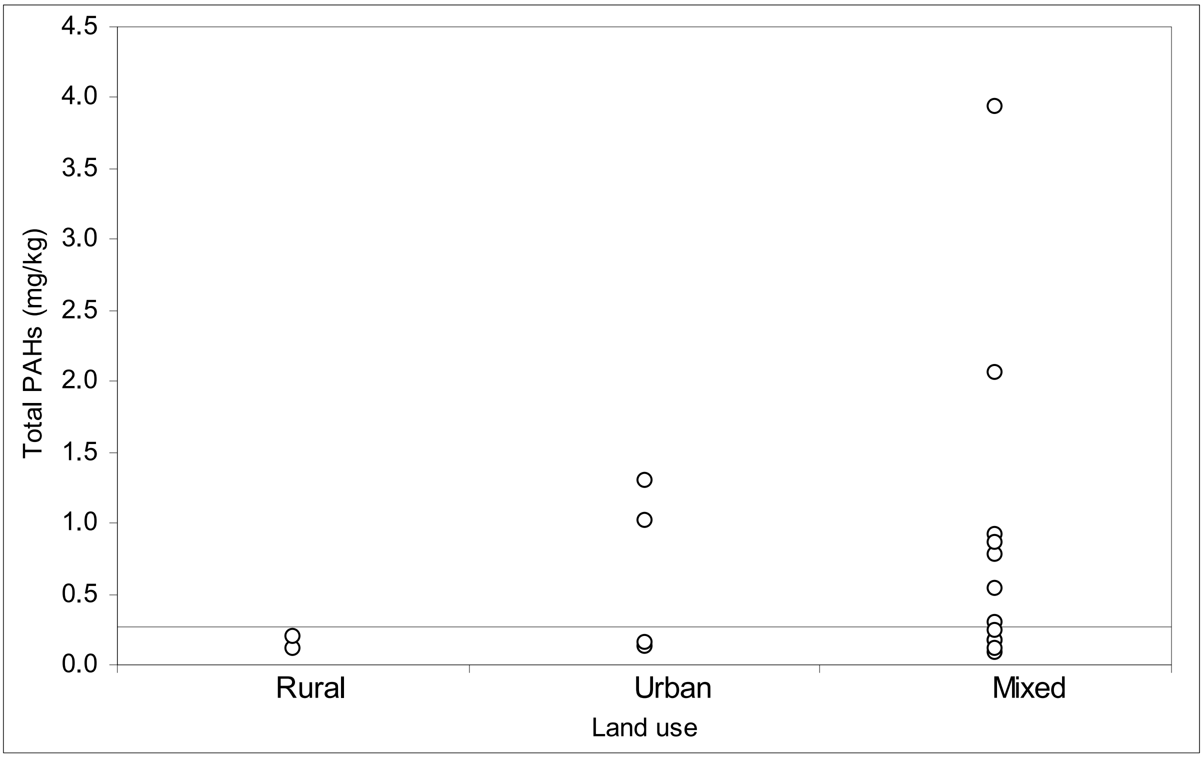

Figure 18: Comparison of total PAH concentrations (normalised to 1% TOC) in sediments from different land uses. Note: solid line is the overall median.

7.6 Comparison to Sediment Quality Guidelines for PAHs

ANZECC (2000) provides sediment quality guidelines for 12 individual PAHs, low molecular weight PAHs, high molecular weight PAHs and total PAHs. The guidelines are provided as concentrations normalised to 1% organic carbon, to adjust for the influence of organic carbon in adsorbing organic compounds to sediment particles. Table 14 compares the ANZECC guidelines for PAHs with the concentrations found in the Styx ICMP area, normalised to 1% total organic carbon. Only samples where PAHs were measured above the detection limit are presented in this table.

The samples from Styx River at Marshlands Road (site 3) and Wilsons Drain (site 11) contained individual PAHs at concentrations above the ANZECC ISQG-low. Phenanthrene was the only compound that exceeded the guidelines that was common to both samples. The ISQG-low for low molecular weight PAHs was also exceeded by both samples and the sample from site 3 also exceeded the ISQG-low for high molecular weight PAHs. There were no exceedances of the ISQG-high guidelines for either individual compounds or groups of compounds.

Table 14: PAH concentrations normalised by total organic carbon content (to 1% TOC) compared to ANZECC guidelines.

	ANZECC guidelines		Site							
	ISQG-low	ISQG-high	12	3	14	7	9	10	17	11
TOC	-	-	1.39	4.61	3.5	1.49	2.87	2.24	5	14.25
Acenaphthene	0.016	0.50	0.004	0.029	0.007	0.011	0.007	0.010	0.007	**0.026**
Acenaphthylene	0.044	0.64	0.004	**0.042**	0.007	0.006	**0.019**	**0.020**	0.007	**0.014**
Anthracene	0.085	1.1	0.004	**0.077**	0.007	0.006	**0.024**	0.010	0.007	**0.084**
Fluorene	0.019	0.54	0.004	0.015	0.007	0.006	0.007	0.010	0.007	**0.074**
Naphthalene	0.16	2.1	0.021	0.150	0.037	0.027	0.036	0.048	0.036	0.028
Phenanthrene	0.24	1.5	**0.022**	**0.308**	**0.019**	**0.011**	**0.105**	**0.132**	**0.104**	**0.478**
Low molecular weight PAHs [1]	0.552	3.16	0.059	**0.620**	0.086	0.067	0.198	0.228	0.169	**0.705**
Benzo[a]anthracene	0.261	1.6	**0.009**	**0.275**	**0.015**	0.006	**0.086**	**0.040**	**0.062**	**0.109**
Benzo[a]pyrene (BAP)	0.43	1.6	0.004	**0.342**	0.007	0.006	**0.114**	**0.091**	**0.074**	**0.117**
Chrysene	0.384	2.8	**0.011**	**0.292**	**0.015**	0.006	**0.109**	**0.064**	**0.064**	**0.123**
Dibenzo[a,h]anthracene	0.063	0.26	0.004	**0.038**	0.007	0.006	**0.015**	0.010	0.007	**0.012**
Fluoranthene	0.60	5.1	**0.033**	**0.683**	**0.025**	**0.018**	**0.200**	**0.141**	**0.120**	**0.362**
Pyrene	0.665	2.6	**0.033**	**0.733**	**0.028**	**0.019**	**0.227**	**0.145**	**0.134**	**0.348**
High molecular weight PAHs [1]	1.7	9.6	0.094	**2.363**	0.098	0.059	0.751	0.490	0.461	1.072
Total PAHs [2]	4.0	45.0	0.18	3.9	0.24	0.16	1.30	1.02	0.92	2.1

Notes: Values in bold are above detection limit. Half of detection limit used for compounds that are below detection. Yellow shading indicates exceedance of ISQG-low, red shading indicates exceedance of ISQG-high. [1] Sum of 6 compounds listed above. [2] Sum of all 16 PAHs measured (half of detection limit used for compounds that are below detection). All data mg/kg.

8.0 INFLUENCE ON INSTREAM ECOLOGY

8.1 Introduction

This section of the report discusses the potential influence of sediment quality on instream ecology, particularly with reference to macroinvertebrates. Aquatic habitat and macroinvertebrate values have been assessed at a large number of sites in the Styx River and Kaputone Stream by Boffa Miskell (2007). Environment Canterbury have macroinvertebrate monitoring sites on the Styx River within the Styx Mill Conservation Reserve (between sites 1 and 2) and in the Kaputone Stream at Belfast Road (site 15). The review of invertebrate information for the Styx ICMP area has been limited to that contained in EOS Ecology (2008) and Boffa Miskell (2007).

8.2 Styx River

Boffa Miskell (2007) report variation in both physical habitat and macroinvertebrate values upstream of Main North Road, with quality ranging from good to very degraded. Downstream of Main North Road, the macroinvertebrate values are poor at all locations in the Styx River until the most downstream location near Hawkins Road, despite continued variation in the physical habitat values.

In the stretch of the Styx River between Styx Mill Reserve and Main North Road, macroinvertebrate communities had moderate taxa richness and the QMCI scores indicated fair water quality (EOS Ecology 2008).

The sediment quality for the Styx River from Sawyers Arms Road to Main North Road was good compared to other locations in the ICMP area and compared to sediment quality guidelines. No samples exceeded the ANZECC (2000) ISQG-low for any metal, and most metals were well below (less than half) their respective guidelines. Furthermore, there were no PAHs detected in samples from this stretch of the river, based on the screening detection limits. The sediments in these locations had a large range of silt-sized particles (9-40%), which are unlikely to be having a detrimental effect on instream biota in this stretch of the river.

At Marshlands Road, PAHs were elevated in the sample and exceeded the ANZECC ISQG-low for several compounds. In this location, there is a chance of adverse effects occurring based on poor sediment quality. However, neither the Boffa Miskell (2007) or EOS Ecology (2008) studies extended downstream to, or beyond, Marshlands Road.

The sediment sample collected at the most upstream location in the Styx River, immediately downstream of Sawyers Arms Road (site 12) exceeded the ISQG-low for both lead and zinc. This indicates the potential for adverse effects on instream biota at this location. However, the biota is more likely to be affected by the overall habitat quality at this location, as the Styx River is ephemeral in these upper reaches. The sampling location was close to dry at the time of sampling and the stream bed was dry less than 5 metres downstream.

8.3 Kaputone Stream

Boffa Miskell (2007) reported the macroinvertebrate values of the Kaputone Stream to be very degraded, while the physical habitat was described as fair, near the sites sampled for sediment quality. EOS Ecology (2008) also reported poor macroinvertebrate community health in two sites at the stream, with MCI scores indicating severe organic pollution. The sediments of the Kaputone Stream were dominated by silt and fine sand (Section 5.2) which may affect habitat quality. Moreover, lead and zinc concentrations were elevated in these sediments compared to other locations. Lead concentrations exceeded the ANZECC ISQG-low but were below the ISQG-high, while zinc concentrations exceeded the upper guideline as well as the lower. Effects can be expected to occasionally occur when metal concentrations are above the ISQG-low but below the ISQG-high, while adverse effects in biota are expected to frequently occur when the ISQG-high is exceeded. The elevated concentrations of zinc may therefore contribute to the poor macroinvertebrate communities observed in these locations.

8.4 Smacks Creek

The sediment sample from Smacks Creek indicated generally high quality, with all metals below sediment quality guidelines. In contrast, EOS Ecology (2008) and Boffa Miskell (2007) reported poor macroinvertebrate community health at the same location. EOS Ecology (2008) found a very low QMCI score at that location, which is indicative of invertebrate communities tolerant of poor conditions and silted habitats. There was a relatively high proportion of silt-sized particles (~40%) in this stream compared to other locations and this may be influencing the macroinvertebrate community.

8.5 Drains

The macroinvertebrate communities living within drains in the Styx ICMP area have been reported by Boffa Miskell (2007) and EOS Ecology (2008) as poor in terms of diversity and the presence of sensitive taxa. The sediment quality within the urban drains was identified as poor based on exceedance of guidelines for lead and zinc. However, the potential effects on macroinvertebrate populations of poor sediment quality in drains may not be discernable from the poor quality of the physical habitat. This is illustrated by the results for Horners Drain, a straight and concrete-sided drain. Lead and zinc concentrations in sediment collected from this drain exceeded the ANZECC ISQG-low and ISQG-high guidelines respectively and the macroinvertebrate community health was rated as very low by EOS Ecology (2008).

9.0 SUMMARY AND CONCLUSIONS

Sediment texture

The texture of sediments can have a strong influence on metal concentrations, as fine particles have a greater surface area (by weight) than coarse particles, and therefore greater capacity for adsorption of metals. The physical characteristics of the sediments collected in the Styx ICMP area were variable but showed texture dominated by mud (silt and clay) or fine sand.

Trace elements

The survey of sediments from the Styx River and Wilsons Drain catchments has shown that the concentrations of trace elements were:

- Variable between sites ranging from a less than two fold variation in nickel concentrations through to an almost twenty fold variation in cadmium, copper, lead and zinc.
- Generally lower in the mainstem of the Styx River compared with those recorded in Kaputone Stream and urban drains (Kruses Drain, un-named drain, Horners Drain).
- Elevated (particularly cadmium and zinc) in the sediments of several sites compared to previously reported soil concentrations suggesting enrichment of the sediments with anthropogenic sources, most likely via stormwater.
- Above the background range in fine particles for local sediments (particularly cadmium, lead and zinc) by up to 20 times, indicating that metal concentrations in sediments of the Styx ICMP area are enriched by other factors to a greater extent than sediment texture.
- Generally lower in sediments from rural land compared to those from urban land with the exception of nickel concentrations which were greater from sites in rural land use areas and chromium which were similar for rural and urban land use area sites.

The concentration of trace elements in sediments from the Styx River ICMP area were generally lower in rural areas compared with other rural catchments in Christchurch and Rangiora with the exception of copper and lead, and in urban areas comparable to results from urban and residential areas in the Heathcote River and Halswell River catchments (particularly copper, zinc and lead).

The 2009 sediment survey indicated the following changes in trace element concentrations from the previous (1980/81) survey:

- Zinc concentrations in sediments increased at 12 out of 16 sites and at six of these sites by more than 50%.
- Increased concentrations of cadmium were recorded at 12 of the 15 sites in 2009 (Cadmium was generally below the detection limit in 1980/81).
- Lead concentrations were at least 50% lower at 5 sites.
- Chromium and nickel concentrations generally increased only marginally with large increases since 1980/81 recorded at a limited number of sites.

Just two sites had a change in mud content of more than 50%, which indicates that a change in sample texture was not likely to have been responsible for the changes in metal concentrations.

A comparison of the trace element concentrations in the sediments of the Styx River and Wilsons Drain catchments with the ANZECC (2000) guidelines showed that:

- Lead and zinc were the only metals to exceed the guidelines.
- Six sites recorded lead concentrations in excess of the ISQG-low.
- Zinc exceeded the ISQG-low at ten sites with five of these sites also exceeding the ISQG-high.
- Only three of the nine sites sampled in the Styx River mainstem recorded metal concentrations in excess of any guidelines.
- All three sites sampled in the Kaputone Stream exceeded the zinc guidelines and two exceeded the lead guidelines. Zinc concentrations exceeded the ISQG-high at two out of the three sites.
- Four sites sampled in 1980/81 continued to exceed ISQG-low guidelines for either lead or zinc when re-sampled in 2009. There was a greater exceedance of the ISQG-high for zinc compared with the 1980 survey.
- At three sites, lead concentrations, which had been above the ISQG-low or high in 1980/81, were lower in 2009 and below the guidelines.

Overall, metal concentrations are elevated at some locations but are similar to those measured in sediments from streams in other local urban areas. Metal concentrations, particularly zinc and lead are sufficiently elevated in some parts of the Styx ICMP area that they may result in adverse environmental effects.

Polycyclic aromatic hydrocarbons

PAHs concentrations in sediments within the Styx ICMP area were above the detection limit in only 8 of the 18 samples analysed. The 2009 survey has shown that the concentrations of PAHs were:

- Highest in the sample from Wilsons Drain (within the Otukaikino Memorial Reserve). Wilsons Drain receives stormwater from the northern motorway however the concentration recorded at this site was substantially higher than recorded in sediments from Curletts Drain, adjacent to the Christchurch Southern Motorway.
- Dominated by fluoranthene, pyrene, phenanthrene, benzo[b]fluoranthene and benzo[j]fluoranthene. Low molecular weight PAHs were generally lower in concentration and detected less often than high molecular weight PAHs.
- Not related to the concentration of total organic carbon in the sediment as previously found, although the data set is limited (few samples recorded PAH concentrations above the detection limits).
- Not related to the proportion of mud in the samples which is consistent with previous findings.
- Low in sediments from rural sites compared to the sediments from urban or mixed land sites. The mixed land use sites generally had the highest concentration of total PAHs.

Sediments from the lower reaches of the Styx River had relatively low PAH concentrations which were similar to, or lower than, those measured in the Halswell River. The sediments from sites below rural areas (e.g., Rhodes Drain and Winters Road Drain) were generally less than those measured in the rural catchment of the Heathcote River and similar or lower to those measured in the Halswell River.

A comparison of the PAH concentrations in the sediments of the Styx River and Wilsons Drain catchments with the ANZECC (2000) guidelines showed that:

- Only samples from the Styx River at Marshlands Road and Wilsons Drain recorded individual PAH compounds at concentrations above the ISQG-low.
- Phenanthrene was the only compound that exceeded the guidelines at both sites.
- The concentration of low molecular weight PAHs was in excess of the ISQG-low at both sites and the sample from the Styx River also exceeded the ISQG-low for high molecular weight PAHs.
- There were no exceedances of the ISQG-high for either individual PAH compounds or PAH groups.

Overall, PAH concentrations are elevated at a limited number of sites in the Styx ICMP area and are similar to those measured in sediments from streams in other local urban areas. However, PAH concentrations are sufficiently high in Wilsons Drain and the Styx River at Marshlands Road that they may result in adverse environmental effects.

Influence on stream ecology

The review of sediment quality in the Styx ICMP area from the 2009 survey in light of recent ecological surveys (particularly relating to benthic communities) indicates that:

- Macroinvertebrate communities in the Styx River immediately downstream of the Smacks Creek confluence (including the Styx Mill Reserve) have only moderate taxa richness despite the sediment quality in this reach of the Styx River being relatively high (and below sediment quality guidelines) compared to other locations in the catchment.
- Lead and zinc concentrations were elevated in the sediments of the Kaputone Stream (and exceeded sediment quality guidelines) consistent with the macroinvertebrate communities which are described as poor or very degraded in this stream.
- Metals in the sediment sample from Smacks Creek were all below guidelines whilst the macroinvertebrate community health has been reported as poor in the same location.
- The generally poor quality of sediments in drains within the Styx ICMP area is consistent with the poor health of macroinvertebrate communities in these drains.

Many of the sites surveyed, particularly within Smacks Creek and the drains, had a relatively high proportion of silt-sized particles and/or poor physical habitat which is likely to contribute to the health of macroinvertebrate communities. Overall, no clear relationship between sediment quality and stream ecology was evident in the Styx ICMP area. It is likely that other factors including stream substrate and physical habitat drive the instream ecology in the Styx River ICMP area.

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APPENDIX A

Report Limitations

REPORT LIMITATIONS

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APPENDIX B

Site Photographs

Site 1: Styx River bottom

Site 1: Styx River downstream

Site 1: Styx River upstream

Site 2: Styx River

Site 2: Styx River downstream

Site 3: Styx River downstream

Site 3: Styx River upstream

Site 4: Styx River downstream

Site 4: Styx River upstream

Site 5: Styx River downstream

Site 5: Styx River upstream

Site 6: Smacks River upstream

Site 7: Kaputone Stream downstream

Site 7: Kaputone Stream upstream

Site 8: Kaputone Stream downstream

Site 8: Kaputone Stream upstream

Site 9: Unnamed Drain downstream

Site 9: Unnamed Drain upstream

Site 10: Kruses Drain sampling

Site 10: Kruses Drain upstream

Site 11: Wilsons Drain substrate

Site 11: Wilsons Drain upstream

Site 12: Styx River

Site 12: Styx River downstream

Site 12: Styx River upstream

Site 14: Styx River downstream

Site 14: Styx River upstream

Site 15: Kaputone Stream downstream

Site 15: Kaputone Stream upstream

Site 16: Styx River SWP inlet

Site 16: Styx River SWP outlet

Site 17: Horners Drain downstream

Site 17: Horners Drain upstream

Site 18: Rhodes Drain downstream

Site18: Rhodes Drain upstream

Site19: Winters Drain downstream

Site19: Winters Drain upstream

Site 20: Spencerville Drain downstream

Site20: Spencerville Drain upstream

Site 21: Kainga Drain downstream

Site 21: Kainga Drain upstream

Site 22: Styx River downstream

Site 23: Styx River upstream

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APPENDIX C

Grain size analysis

Table 1: Sediment sample texture as measured by sieving.

Site	Waterway	Dry matter (%)	Gravel (% > 2 mm)	Sand (% 0.063 -2 mm)	Mud (% < 0.063 mm)
12	Styx	29	2.8	57.5	39.7
1	Styx	50	1.1	77.4	21.5
2	Styx	67	0.2	93.7	6.1
13	Styx	33	16.2	55	28.8
3	Styx	61	2.5	82.9	14.6
14	Styx	38	4	56.3	39.7
4	Styx	22	1.1	43.9	55.0
22	Styx	65	0.2	91.9	7.8
5	Styx	53	27.3	71.5	1.2
6	Smacks	9.1	14.2	49.0	36.8
7	Kaputone	19	5.0	46.2	48.8
8	Kaputone	15	5.3	57.5	37.2
9	Unnamed	68	53.1	50.9	<0.1
10	Kruses	54	16.5	62.6	20.9
11	Wilsons	25	2.3	28.3	69.4
15	Kaputone	28	46.68	35.40	8.73
17	Horners Drain	29	81.02	15.38	2.56
18	Rhodes Drain	37	56.23	28.53	9.04
20	Spencerville	34	59.42	31.78	7.79

;

Table 2: Sediment texture classified by Wentworth scale (data from particle size analyser).

Site	Waterway	Clay (< 2 µm)	Silt (2 - 63 µm)	Very fine sand (63 - 125 µm)	Fine sand (125 - 250 µm)	Medium sand (250 - 500 µm)	Coarse sand (500 - 1000 µm)	Very coarse sand (1000 - 2000 µm)
12	Styx	0.00	40.53	22.49	18.92	9.39	5.45	3.21
1	Styx	0.00	25.41	26.96	31.88	10.74	2.48	2.51
2	Styx	0.00	9.49	22.57	45.34	21.66	0.94	0.00
13	Styx	0.03	47.93	21.65	16.5	8.31	4.27	1.32
3	Styx	0.03	25.87	17.90	38.68	17.11	0.40	0.00
14	Styx	0.03	49.91	21.84	19.15	8.23	1.61	0.24
4	Styx	0.00	53.42	20.49	15.70	7.76	2.42	0.21
22	Styx	0.00	8.32	7.08	53.38	30.63	0.59	0.00
5	Styx	0.00	19.44	9.19	35.09	30.18	4.98	1.13
6	Smacks	0.00	43.95	15.37	13.81	12.49	10.32	4.08
7	Kaputone	0.00	40.43	21.08	17.45	10.60	6.92	3.49
15	Kaputone	0	46.68	20.11	15.29	8.73	6.63	2.58
8	Kaputone	0.02	9.49	12.63	62.30	15.55	0.00	0.00
9	Unnamed	0.00	9.32	5.60	12.13	19.37	31.54	22.06
10	Kruses	0.02	7.75	11.36	63.49	17.39	0.01	0.00
11	Wilsons	0.03	67.34	14.84	6.86	4.63	4.37	1.93
17	Horners	0.26	80.76	10.1	5.28	2.56	1.03	0.04
18	Rhodes	0.31	55.92	14.62	13.91	9.04	4.77	1.45
20	Spencerville	0.05	59.37	16.45	15.33	7.79	1.02	0

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APPENDIX D

Laboratory sheets

Hill Laboratories
BETTER TESTING BETTER RESULTS

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ANALYSIS REPORT

Client:	Golder Associates (NZ) Ltd	**Lab No:**	681482 SPv5
Contact:	A Wilkes	**Date Registered:**	27-Feb-2009
	C/- Golder Associates (NZ) Ltd	**Date Reported:**	28-Apr-2009
	PO Box 2281	**Quote No:**	33836
	Christchurch Mail Centre	**Order No:**	087813152
	CHRISTCHURCH 8140	**Client Reference:**	GANZL-CCC-SED
		Submitted By:	Ms J Gadd

Amended Report

This report replaces an earlier report issued on the 09 Apr 2009 at 9:33 am
At the client's request, sieve analysis has been added to samples 681482.1, .2, .4, .5 and .7.

Sample Type: Sediment

Sample Name:		Styx # 14 25-Feb-2009 10:45 am	Styx # 15 18-Feb-2009 10:30 am	Styx # 17 19-Feb-2009 10:30 am	Styx # 18 19-Feb-2009 2:20 pm	Styx # 20 18-Feb-2009 9:20 am
Lab Number:		681482.1	681482.2	681482.4	681482.5	681482.7
Individual Tests						
Dry Matter	g/100g as rcvd	38	28	29	37	34
Fraction >/= 2 mm*	g/100g dry wt	4.0	25.0	0.8	21.7	1.6
Fraction < 2 mm, >/= 63 µm*	g/100g dry wt	56.3	55.0	13.8	21.7	46.8
Fraction < 63 µm*	g/100g dry wt	39.7	20.0	85.4	56.6	51.5
Total Organic Carbon	g/100g dry wt	3.5	-	5.0	4.9	3.2
Heavy metal, trace level As,Cd,Cr,Cu,Ni,Pb,Zn						
Total Recoverable Arsenic	mg/kg dry wt	6.6	9.6	13	15	14
Total Recoverable Cadmium	mg/kg dry wt	0.20	0.28	0.59	0.13	0.087
Total Recoverable Chromium	mg/kg dry wt	21	21	27	21	15
Total Recoverable Copper	mg/kg dry wt	17	14	45	16	9.1
Total Recoverable Lead	mg/kg dry wt	27	46	93	26	14
Total Recoverable Nickel	mg/kg dry wt	12	11	20	16	12
Total Recoverable Zinc	mg/kg dry wt	230	240	760	87	58
Polycyclic Aromatic Hydrocarbons Screening in Soil						
Acenaphthene	mg/kg dry wt	< 0.052	-	< 0.072	< 0.056	< 0.065
Acenaphthylene	mg/kg dry wt	< 0.052	-	< 0.072	< 0.056	< 0.065
Anthracene	mg/kg dry wt	< 0.052	-	< 0.072	< 0.056	< 0.065
Benzo[a]anthracene	mg/kg dry wt	0.053	-	0.31	< 0.056	< 0.065
Benzo[a]pyrene (BAP)	mg/kg dry wt	< 0.052	-	0.37	< 0.056	< 0.065
Benzo[b]fluoranthene + Benzo[j] fluoranthene	mg/kg dry wt	0.11	-	0.74	< 0.056	< 0.065
Benzo[g,h,i]perylene	mg/kg dry wt	< 0.052	-	0.26	< 0.056	< 0.065
Benzo[k]fluoranthene	mg/kg dry wt	< 0.052	-	0.24	< 0.056	< 0.065
Chrysene	mg/kg dry wt	0.052	-	0.32	< 0.056	< 0.065
Dibenzo[a,h]anthracene	mg/kg dry wt	< 0.052	-	< 0.072	< 0.056	< 0.065
Fluoranthene	mg/kg dry wt	0.086	-	0.60	< 0.056	< 0.065
Fluorene	mg/kg dry wt	< 0.052	-	< 0.072	< 0.056	< 0.065
Indeno(1,2,3-c,d)pyrene	mg/kg dry wt	< 0.052	-	0.19	< 0.056	< 0.065
Naphthalene	mg/kg dry wt	< 0.26	-	< 0.36	< 0.28	< 0.33
Phenanthrene	mg/kg dry wt	0.068	-	0.52	< 0.056	< 0.065
Pyrene	mg/kg dry wt	0.099	-	0.67	< 0.056	< 0.065

Sample Type: Sediment						
Sample Name:		Styx # 1 18-Feb-2009 11:45 am	Styx # 2 19-Feb-2009 1:10 pm	Styx # 3 19-Feb-2009 3:00 pm	Styx # 4 25-Feb-2009 10:30 am	Styx # 5 25-Feb-2009 9:00 am
Lab Number:		681482.9	681482.10	681482.11	681482.12	681482.13
Individual Tests						
Dry Matter	g/100g as rcvd	50	67	61	22	53
Fraction >/= 2 mm*	g/100g dry wt	1.1	0.2	2.5	1.1	27.3
Fraction < 2 mm, >/= 63 µm*	g/100g dry wt	77.4	93.7	82.9	43.9	71.5
Fraction < 63 µm*	g/100g dry wt	21.5	6.1	14.6	55.0	1.2
Total Organic Carbon	g/100g dry wt	1.3	0.44	1.2	7.2	1.0
Heavy metal, trace level As,Cd,Cr,Cu,Ni,Pb,Zn						
Total Recoverable Arsenic	mg/kg dry wt	1.4	1.3	2.7	11	3.9
Total Recoverable Cadmium	mg/kg dry wt	0.063	0.088	0.067	0.37	0.052
Total Recoverable Chromium	mg/kg dry wt	12	10	12	30	12
Total Recoverable Copper	mg/kg dry wt	8.6	3.5	6.4	26	4.4
Total Recoverable Lead	mg/kg dry wt	16	6.7	20	49	8.6
Total Recoverable Nickel	mg/kg dry wt	9.5	7.7	7.8	14	9.0
Total Recoverable Zinc	mg/kg dry wt	54	64	86	350	63
Polycyclic Aromatic Hydrocarbons Screening in Soil						
Acenaphthene	mg/kg dry wt	< 0.038	< 0.034	< 0.035	< 0.12	< 0.053
Acenaphthylene	mg/kg dry wt	< 0.038	< 0.034	0.050	< 0.12	< 0.053
Anthracene	mg/kg dry wt	< 0.038	< 0.034	0.092	< 0.12	< 0.053
Benzo[a]anthracene	mg/kg dry wt	< 0.038	< 0.034	0.33	< 0.12	< 0.053
Benzo[a]pyrene (BAP)	mg/kg dry wt	< 0.038	< 0.034	0.41	< 0.12	< 0.053
Benzo[b]fluoranthene + Benzo[j] fluoranthene	mg/kg dry wt	< 0.038	< 0.034	0.48	< 0.12	< 0.053
Benzo[g,h,i]perylene	mg/kg dry wt	< 0.038	< 0.034	0.28	< 0.12	< 0.053
Benzo[k]fluoranthene	mg/kg dry wt	< 0.038	< 0.034	0.21	< 0.12	< 0.053
Chrysene	mg/kg dry wt	< 0.038	< 0.034	0.35	< 0.12	< 0.053
Dibenzo[a,h]anthracene	mg/kg dry wt	< 0.038	< 0.034	0.045	< 0.12	< 0.053
Fluoranthene	mg/kg dry wt	< 0.038	< 0.034	0.82	< 0.12	< 0.053
Fluorene	mg/kg dry wt	< 0.038	< 0.034	< 0.035	< 0.12	< 0.053
Indeno(1,2,3-c,d)pyrene	mg/kg dry wt	< 0.038	< 0.034	0.17	< 0.12	< 0.053
Naphthalene	mg/kg dry wt	< 0.19	< 0.17	< 0.18	< 0.56	< 0.27
Phenanthrene	mg/kg dry wt	< 0.038	< 0.034	0.37	< 0.12	< 0.053
Pyrene	mg/kg dry wt	< 0.038	< 0.034	0.88	< 0.12	< 0.053

Sample Name:		Styx # 5a 25-Feb-2009 9:30 am	Styx # 6 19-Feb-2009 11:30 am	Styx # 7 18-Feb-2009 11:15 am	Styx # 8 19-Feb-2009 3:45 pm	Styx # 9a 25-Feb-2009 12:00 pm
Lab Number:		681482.14	681482.15	681482.16	681482.17	681482.18
Individual Tests						
Dry Matter	g/100g as rcvd	65	9.1	19	15	68
Fraction >/= 2 mm*	g/100g dry wt	0.2	14.2	5.0	5.3	53.1
Fraction < 2 mm, >/= 63 µm*	g/100g dry wt	91.9	49.0	46.2	57.5	50.9
Fraction < 63 µm*	g/100g dry wt	7.8	36.8	48.8	37.2	< 0.1
Total Organic Carbon	g/100g dry wt	0.43	15	9.6	14	2.2
Heavy metal, trace level As,Cd,Cr,Cu,Ni,Pb,Zn						
Total Recoverable Arsenic	mg/kg dry wt	4.1	13	8.8	8.6	16
Total Recoverable Cadmium	mg/kg dry wt	0.022	0.94	0.55	0.35	0.32
Total Recoverable Chromium	mg/kg dry wt	11	40	17	39	15
Total Recoverable Copper	mg/kg dry wt	3.2	31	21	26	28
Total Recoverable Lead	mg/kg dry wt	5.4	20	72	52	200
Total Recoverable Nickel	mg/kg dry wt	8.6	8.0	11	10	11
Total Recoverable Zinc	mg/kg dry wt	33	76	610	430	570
Polycyclic Aromatic Hydrocarbons Screening in Soil						
Acenaphthene	mg/kg dry wt	< 0.037	< 0.18	< 0.11	< 0.12	< 0.031
Acenaphthylene	mg/kg dry wt	< 0.037	< 0.18	< 0.11	< 0.12	0.041
Anthracene	mg/kg dry wt	< 0.037	< 0.18	< 0.11	< 0.12	0.053
Benzo[a]anthracene	mg/kg dry wt	< 0.037	< 0.18	< 0.11	< 0.12	0.19

Sample Type: Sediment						
Sample Name:		Styx # 5a 25-Feb-2009 9:30 am	Styx # 6 19-Feb-2009 11:30 am	Styx # 7 18-Feb-2009 11:15 am	Styx # 8 19-Feb-2009 3:45 pm	Styx # 9a 25-Feb-2009 12:00 pm
Lab Number:		681482.14	681482.15	681482.16	681482.17	681482.18
Polycyclic Aromatic Hydrocarbons Screening in Soil						
Benzo[a]pyrene (BAP)	mg/kg dry wt	< 0.037	< 0.18	< 0.11	< 0.12	0.25
Benzo[b]fluoranthene + Benzo[j] fluoranthene	mg/kg dry wt	< 0.037	< 0.18	0.11	< 0.12	0.26
Benzo[g,h,i]perylene	mg/kg dry wt	< 0.037	< 0.18	< 0.11	< 0.12	0.22
Benzo[k]fluoranthene	mg/kg dry wt	< 0.037	< 0.18	< 0.11	< 0.12	0.18
Chrysene	mg/kg dry wt	< 0.037	< 0.18	< 0.11	< 0.12	0.24
Dibenzo[a,h]anthracene	mg/kg dry wt	< 0.037	< 0.18	< 0.11	< 0.12	0.032
Fluoranthene	mg/kg dry wt	< 0.037	< 0.18	0.17	< 0.12	0.44
Fluorene	mg/kg dry wt	< 0.037	< 0.18	< 0.11	< 0.12	< 0.031
Indeno(1,2,3-c,d)pyrene	mg/kg dry wt	< 0.037	< 0.18	< 0.11	< 0.12	0.12
Naphthalene	mg/kg dry wt	< 0.19	< 0.90	< 0.52	< 0.60	< 0.16
Phenanthrene	mg/kg dry wt	< 0.037	< 0.18	0.11	< 0.12	0.23
Pyrene	mg/kg dry wt	< 0.037	< 0.18	0.18	< 0.12	0.50

Sample Name:		Styx # 10 19-Feb-2009 9:00 am	Styx # 11 25-Feb-2009 11:30 am	Styx # 12 25-Feb-2009 12:20 pm	Styx # 13 19-Feb-2009 1:50 pm	
Lab Number:		681482.19	681482.20	681482.21	681482.22	
Individual Tests						
Dry Matter	g/100g as rcvd	54	25	29	33	-
Fraction >/= 2 mm*	g/100g dry wt	16.5	2.3	2.8	16.2	-
Fraction < 2 mm, >/= 63 µm*	g/100g dry wt	62.6	28.3	57.5	55.0	-
Fraction < 63 µm*	g/100g dry wt	20.9	69.4	39.7	28.8	-
Total Organic Carbon	g/100g dry wt	2.2	6.9	7.9	5.2	-
Heavy metal, trace level As,Cd,Cr,Cu,Ni,Pb,Zn						
Total Recoverable Arsenic	mg/kg dry wt	17	14	4.5	6.3	-
Total Recoverable Cadmium	mg/kg dry wt	0.24	0.28	0.25	0.20	-
Total Recoverable Chromium	mg/kg dry wt	18	28	15	15	-
Total Recoverable Copper	mg/kg dry wt	23	24	29	13	-
Total Recoverable Lead	mg/kg dry wt	53	48	74	23	-
Total Recoverable Nickel	mg/kg dry wt	11	14	10	12	-
Total Recoverable Zinc	mg/kg dry wt	700	330	220	130	-
Polycyclic Aromatic Hydrocarbons Screening in Soil						
Acenaphthene	mg/kg dry wt	< 0.042	0.18	< 0.065	< 0.060	-
Acenaphthylene	mg/kg dry wt	0.044	0.10	< 0.065	< 0.060	-
Anthracene	mg/kg dry wt	< 0.042	0.58	< 0.065	< 0.060	-
Benzo[a]anthracene	mg/kg dry wt	0.087	0.75	0.073	< 0.060	-
Benzo[a]pyrene (BAP)	mg/kg dry wt	0.20	0.81	< 0.065	< 0.060	-
Benzo[b]fluoranthene + Benzo[j] fluoranthene	mg/kg dry wt	0.24	0.86	0.084	< 0.060	-
Benzo[g,h,i]perylene	mg/kg dry wt	0.18	0.38	< 0.065	< 0.060	-
Benzo[k]fluoranthene	mg/kg dry wt	0.13	0.49	< 0.065	< 0.060	-
Chrysene	mg/kg dry wt	0.14	0.85	0.084	< 0.060	-
Dibenzo[a,h]anthracene	mg/kg dry wt	< 0.042	0.085	< 0.065	< 0.060	-
Fluoranthene	mg/kg dry wt	0.31	2.5	0.26	< 0.060	-
Fluorene	mg/kg dry wt	< 0.042	0.51	< 0.065	< 0.060	-
Indeno(1,2,3-c,d)pyrene	mg/kg dry wt	0.11	0.26	< 0.065	< 0.060	-
Naphthalene	mg/kg dry wt	< 0.21	< 0.39	< 0.33	< 0.30	-
Phenanthrene	mg/kg dry wt	0.29	3.3	0.17	< 0.060	-
Pyrene	mg/kg dry wt	0.32	2.4	0.26	< 0.060	-

Analyst's Comments

Appendix No.1 - Particle Size Results

Appendix No.2 - Particle Size Results

Appendix No.3 - Particle Size Results

Analyst's Comments

Appendix No.4 - Particle Size Results

Appendix No.5 - Particle Size Results

Appendix No.6 - Particle Size Results

Appendix No.7 - Particle Size Results

Appendix No.8 - Particle Size Results

Appendix No.9 - Particle Size Results

Appendix No.10 - Particle Size Results

Appendix No.11 - Particle Size Results

Appendix No.12 - Particle Size Results

Appendix No.13 - Particle Size Results

Appendix No.14 - Particle Size Results

Appendix No.15 - Particle Size Results

Appendix No.16 - Particle Size Results

Appendix No.17 - Particle Size Results

Appendix No.18 - Particle Size Results

Appendix No.19 - Particle Size Results

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Sediment

Test	Method Description	Default Detection Limit	Samples
Environmental Solids Sample Preparation	Air dried at 35°C and sieved, <2mm fraction.	-	1-2, 4-5, 7, 9-22
Heavy metal, trace level As,Cd,Cr,Cu,Ni,Pb,Zn	Dried sample, <2mm fraction. Nitric/Hydrochloric acid digestion, ICP-MS, trace level.	-	1-2, 4-5, 7, 9-22
Polycyclic Aromatic Hydrocarbons Screening in Soil	Sonication extraction, Dilution or SPE cleanup (if required), GC-MS SIM analysis	-	1, 4-5, 7, 9-22
Dry Matter (Env)	Dried at 103°C (removes 3-5% more water than air dry) for 18hr, gravimetry.	0.10 g/100g as rcvd	1, 4-5, 7, 9-22
Dry Matter	Drying for 16 hours at 103°C, gravimetry (Free water removed before analysis).	0.10 g/100g as rcvd	1-2, 4-5, 7, 9-22
Total Recoverable digestion	Nitric / hydrochloric acid digestion. US EPA 200.2.	-	1-2, 4-5, 7, 9-22
Fraction < 2 mm, >/= 63 µm*	Wet sieving, 2.00 mm and 63 µm sieves, gravimetry (calculation by difference).	0.1 g/100g dry wt	1-2, 4-5, 7, 9-22
Fraction < 63 µm*	Wet sieving, 63 µm sieve, gravimetry (calculation by difference).	0.1 g/100g dry wt	1-2, 4-5, 7, 9-22
Particle size analysis*	Malvern Laser Sizer particle size analysis. Subcontracted to Earth Sciences Department, Waikato University, Hamilton.	-	1-2, 4-5, 7, 9-22
Total Organic Carbon	Acid pretreatment to remove carbonates if present, Elementar Combustion Analyser.	0.050 g/100g dry wt	1, 4-5, 7, 9-22

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

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Carole Rodgers-Carroll BA, NZCS
Client Services Manager - Environmental Division

MALVERN INSTRUMENTS

MASTERSIZER 2000

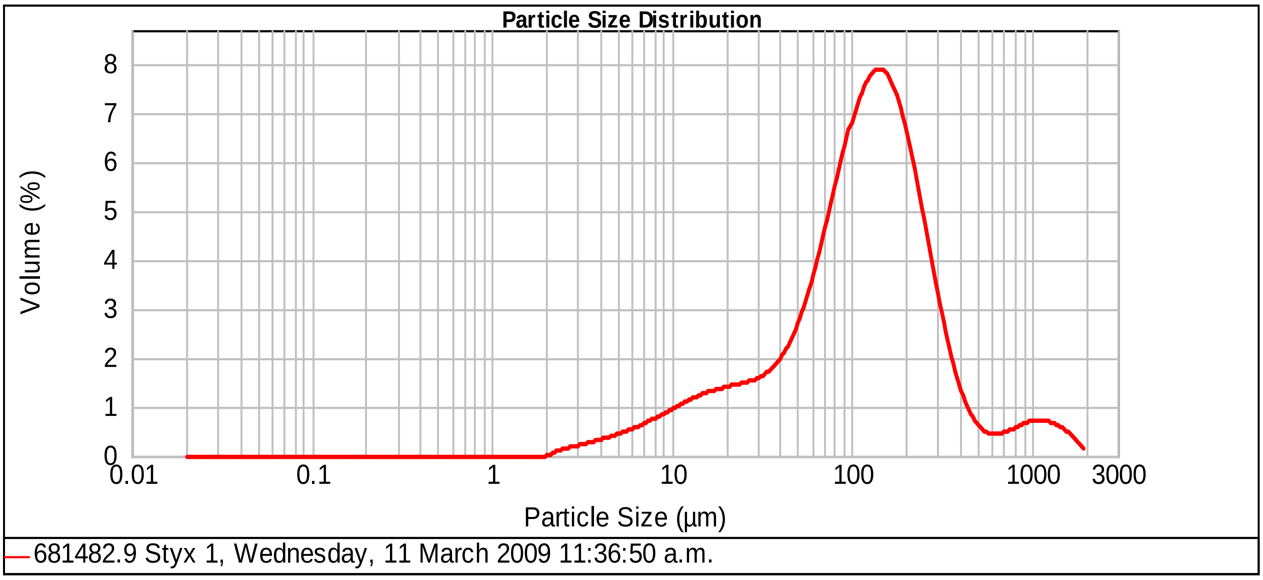
Result Analysis Report

Sample Name: 681482.9 Styx 1	**SOP Name:** Marine Sediment	**Measured:** Wednesday, 11 March 2009 11:36:50 a.m.
Sample Source & type:	**Measured by:** rodgers	**Analysed:** Wednesday, 11 March 2009 11:36:51 a.m.
Sample bulk lot ref: 2009023/1	**Result Source:** Measurement	

Particle Name: Marine Sediment	**Accessory Name:** Hydro 2000G (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 1.500	**Absorption:** 0	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 18.14 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 0.326 %	**Result Emulation:** Off

Concentration: 0.1218 %Vol	**Span :** 2.445	**Uniformity:** 0.973	**Result units:** Volume
Specific Surface Area: 0.129 m²/g	**Surface Weighted Mean D[3,2]:** 46.554 um	**Vol. Weighted Mean D[4,3]:** 175.910 um	

d(0.1): 20.099 um **d(0.5): 119.266 um** **d(0.9): 311.674 um**



Size (µm)	Volume In %
0.050	
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	0.00

Size (µm)	Volume In %
0.980	
2.000	0.00
3.900	0.77
7.800	2.32
15.600	4.66
31.000	6.50
37.000	1.98

Size (µm)	Volume In %
37.000	
44.000	2.28
53.000	3.10
63.000	3.80
74.000	4.58
88.000	6.20
105.000	7.64

Size (µm)	Volume In %
105.000	
125.000	8.54
149.000	9.07
177.000	8.66
210.000	7.71
250.000	6.44
300.000	4.94

Size (µm)	Volume In %
300.000	
350.000	2.79
420.000	1.99
500.000	1.02
590.000	0.57
710.000	0.55
840.000	0.60

Size (µm)	Volume In %
840.000	
1000.000	0.76
2000.000	2.51

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name:
681482.10 Styx 2

SOP Name:
Marine Sediment

Measured:
Wednesday, 11 March 2009 11:53:13 a.m.

Sample Source & type:

Measured by:
rodgers

Analysed:
Wednesday, 11 March 2009 11:53:14 a.m.

Sample bulk lot ref:
2009023/2

Result Source:
Measurement

Particle Name:
Marine Sediment

Accessory Name:
Hydro 2000G (A)

Analysis model:
General purpose

Sensitivity:
Enhanced

Particle RI:
1.500

Absorption:
0

Size range:
0.020 to 2000.000 um

Obscuration:
19.08 %

Dispersant Name:
Water

Dispersant RI:
1.330

Weighted Residual:
0.553 %

Result Emulation:
Off

Concentration:
0.2129 %Vol

Span :
1.575

Uniformity:
0.49

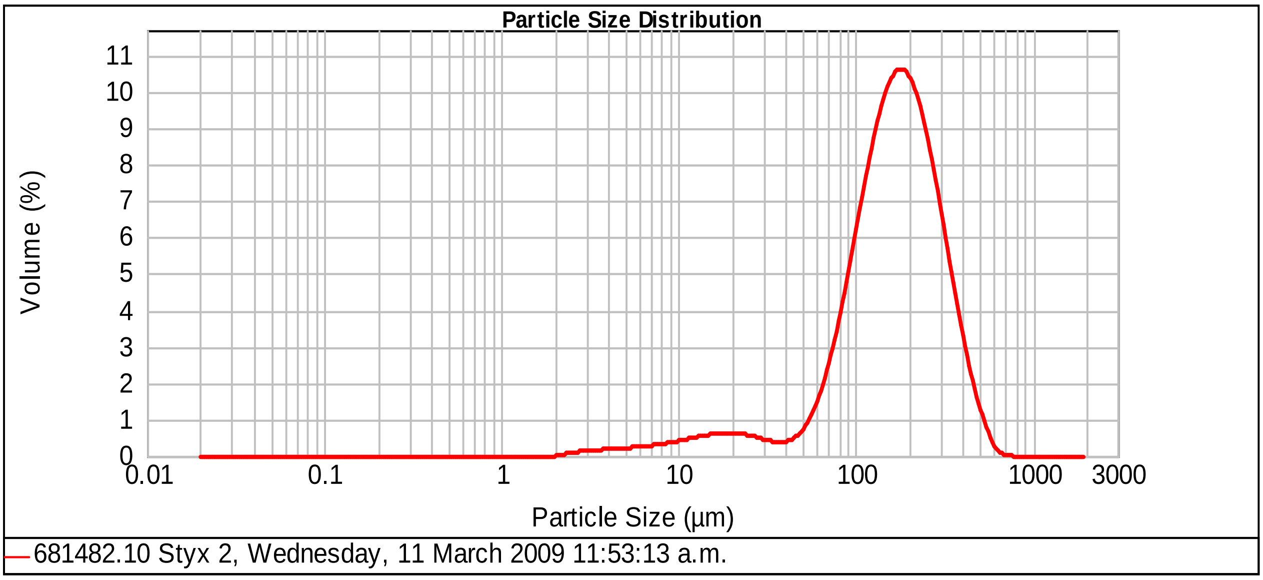
Result units:
Volume

Specific Surface Area:
0.0783 m²/g

Surface Weighted Mean D[3,2]:
76.623 um

Vol. Weighted Mean D[4,3]:
182.365 um

d(0.1): 65.560 um **d(0.5): 165.243 um** **d(0.9): 325.784 um**



Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.00
2.000	0.49
3.900	1.09
7.800	2.10
15.600	2.61
31.000	0.46
37.000	

Size (µm)	Volume In %
37.000	0.46
44.000	0.80
53.000	1.48
63.000	2.50
74.000	4.41
88.000	6.73
105.000	

Size (µm)	Volume In %
105.000	8.93
125.000	10.92
149.000	11.80
177.000	11.73
210.000	10.89
250.000	9.27
300.000	

Size (µm)	Volume In %
300.000	5.78
350.000	4.42
420.000	2.19
500.000	0.82
590.000	0.12
710.000	0.00
840.000	

Size (µm)	Volume In %
840.000	0.00
1000.000	0.00
2000.000	

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name:
681482.11 Styx 3

Sample Source & type:

Sample bulk lot ref:
2009023/3

SOP Name:
Marine Sediment

Measured by:
rodgers

Result Source:
Measurement

Measured:
Thursday, 12 March 2009 9:54:57 a.m.

Analysed:
Thursday, 12 March 2009 9:54:59 a.m.

Particle Name:
Marine Sediment

Particle RI:
1.500

Dispersant Name:
Water

Accessory Name:
Hydro 2000G (A)

Absorption:
0

Dispersant RI:
1.330

Analysis model:
General purpose

Size range:
0.020 to 2000.000 um

Weighted Residual:
0.630 %

Sensitivity:
Enhanced

Obscuration:
16.43 %

Result Emulation:
Off

Concentration:
0.0851 %Vol

Specific Surface Area:
0.16 m²/g

Span :
2.010

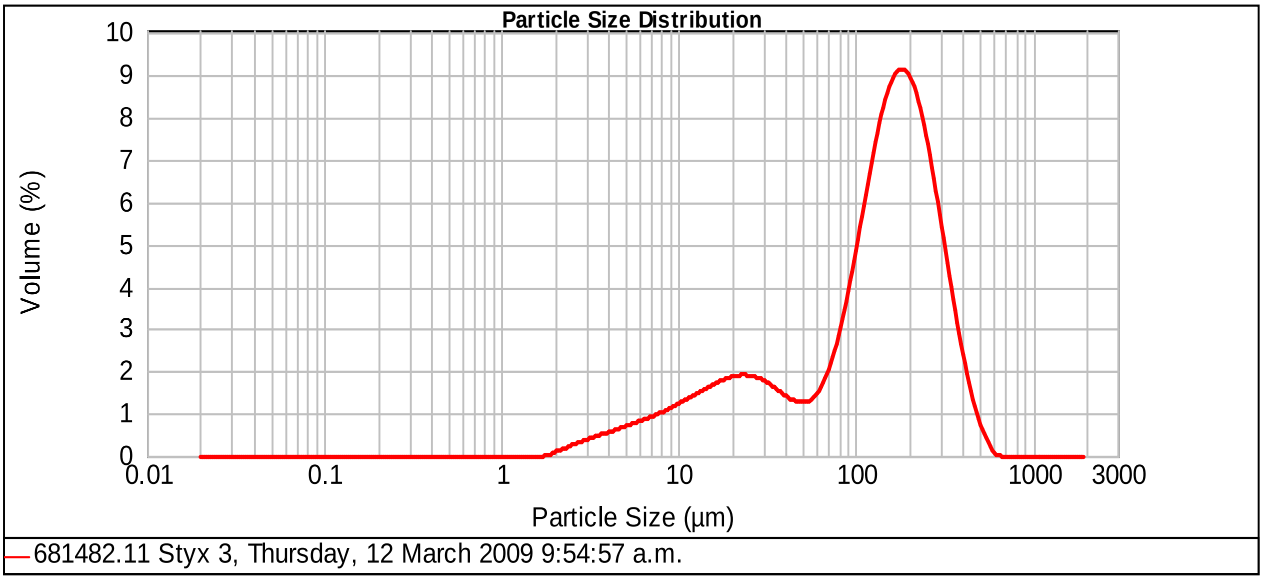
Surface Weighted Mean D[3,2]:
37.499 um

Uniformity:
0.617

Vol. Weighted Mean D[4,3]:
150.523 um

Result units:
Volume

d(0.1): 14.213 um **d(0.5):** 141.234 um **d(0.9):** 298.032 um



Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.03
2.000	1.42
3.900	3.48
7.800	6.07
15.600	8.29
31.000	1.89
37.000	

Size (µm)	Volume In %
37.000	1.59
44.000	1.54
53.000	1.59
63.000	2.05
74.000	3.38
88.000	5.25
105.000	

Size (µm)	Volume In %
105.000	7.22
125.000	9.14
149.000	10.09
177.000	10.12
210.000	9.33
250.000	7.75
300.000	

Size (µm)	Volume In %
300.000	4.63
350.000	3.30
420.000	1.43
500.000	0.40
590.000	0.00
710.000	0.00
840.000	

Size (µm)	Volume In %
840.000	0.00
1000.000	0.00
2000.000	

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name:
681482.12 Styx4

SOP Name:
Marine Sediment

Measured:
Thursday, 12 March 2009 11:03:23 a.m.

Sample Source & type:

Measured by:
rodgers

Analysed:
Thursday, 12 March 2009 11:03:24 a.m.

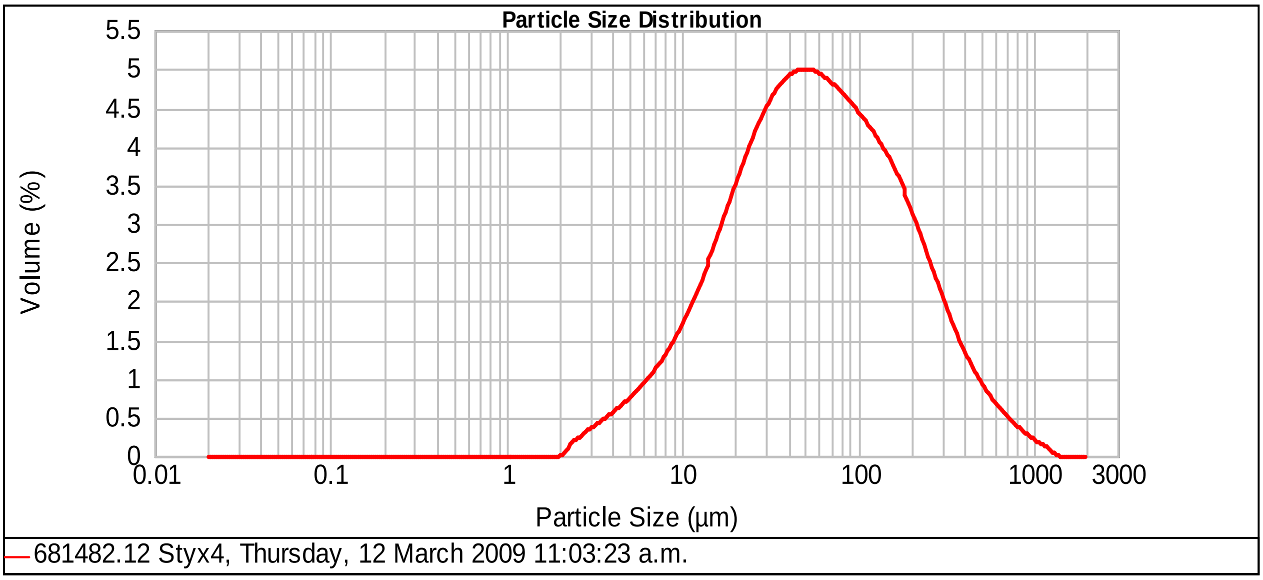
Sample bulk lot ref:
2009023/4

Result Source:
Measurement

Particle Name:	**Accessory Name:**	**Analysis model:**	**Sensitivity:**
Marine Sediment	Hydro 2000G (A)	General purpose	Enhanced
Particle RI:	**Absorption:**	**Size range:**	**Obscuration:**
1.500	0	0.020 to 2000.000 um	19.86 %
Dispersant Name:	**Dispersant RI:**	**Weighted Residual:**	**Result Emulation:**
Water	1.330	0.435 %	Off

Concentration:	**Span :**	**Uniformity:**	**Result units:**
0.0821 %Vol	4.302	1.4	Volume
Specific Surface Area:	**Surface Weighted Mean D[3,2]:**	**Vol. Weighted Mean D[4,3]:**	
0.211 m²/g	28.460 um	106.344 um	

d(0.1): 12.126 um **d(0.5):** 56.671 um **d(0.9):** 255.924 um



Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.00
2.000	1.24
3.900	3.93
7.800	8.86
15.600	16.68
31.000	5.45
37.000	

Size (µm)	Volume In %
37.000	5.57
44.000	6.08
53.000	5.61
63.000	5.11
74.000	5.32
88.000	5.19
105.000	

Size (µm)	Volume In %
105.000	4.87
125.000	4.60
149.000	4.15
177.000	3.69
210.000	3.26
250.000	2.81
300.000	

Size (µm)	Volume In %
300.000	1.91
350.000	1.77
420.000	1.27
500.000	0.90
590.000	0.74
710.000	0.46
840.000	

Size (µm)	Volume In %
840.000	0.32
1000.000	0.21
2000.000	

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

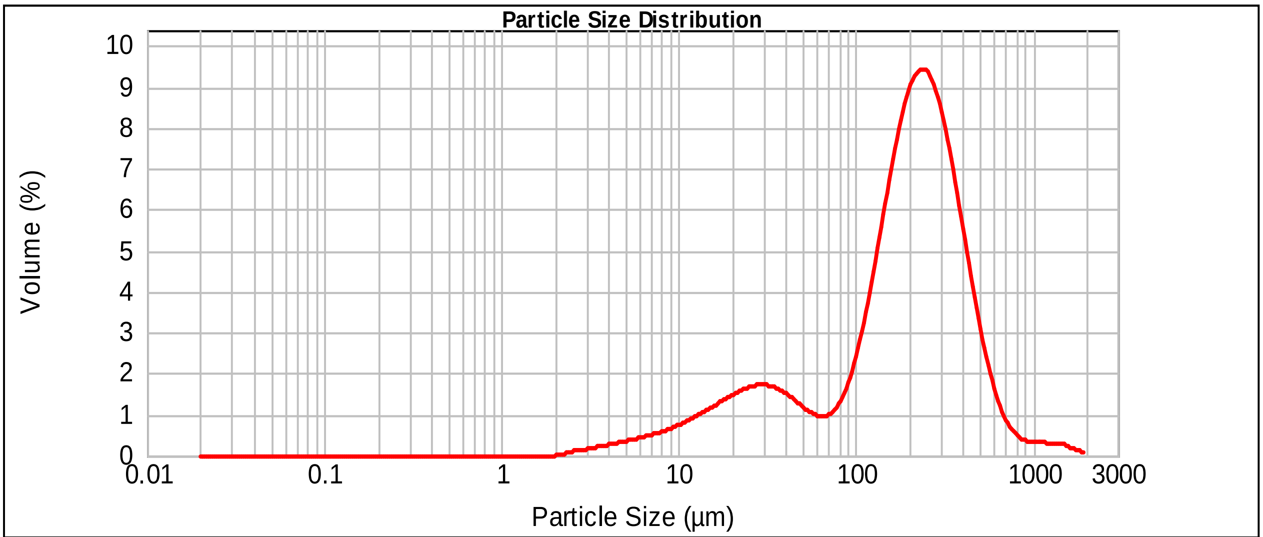
Result Analysis Report

Sample Name: 681482.13 Styx 5	**SOP Name:** Marine Sediment	**Measured:** Thursday, 12 March 2009 11:16:01 a.m.
Sample Source & type:	**Measured by:** rodgers	**Analysed:** Thursday, 12 March 2009 11:16:02 a.m.
Sample bulk lot ref: 2009023/5	**Result Source:** Measurement	

Particle Name: Marine Sediment	**Accessory Name:** Hydro 2000G (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 1.500	**Absorption:** 0	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 13.83 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 0.739 %	**Result Emulation:** Off

Concentration: 0.1152 %Vol	**Span :** 2.027	**Uniformity:** 0.656	**Result units:** Volume
Specific Surface Area: 0.102 m²/g	**Surface Weighted Mean D[3,2]:** 58.839 um	**Vol. Weighted Mean D[4,3]:** 228.834 um	

d(0.1): 23.339 um **d(0.5):** 199.727 um **d(0.9):** 428.241 um



681482.13 Styx 5, Thursday, 12 March 2009 11:16:01 a.m.

Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.00
2.000	0.56
3.900	1.80
7.800	3.87
15.600	6.92
31.000	1.94
37.000	

Size (µm)	Volume In %
37.000	1.70
44.000	1.51
53.000	1.14
63.000	1.03
74.000	1.49
88.000	2.53
105.000	

Size (µm)	Volume In %
105.000	4.14
125.000	6.29
149.000	8.27
177.000	9.81
210.000	10.72
250.000	10.74
300.000	

Size (µm)	Volume In %
300.000	7.82
350.000	7.11
420.000	4.51
500.000	2.52
590.000	1.44
710.000	0.62
840.000	

Size (µm)	Volume In %
840.000	0.40
1000.000	1.13
2000.000	

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name:
681482.14 Styx 5a

SOP Name:
Marine Sediment

Measured:
Thursday, 12 March 2009 11:29:57 a.m.

Sample Source & type:

Measured by:
rodgers

Analysed:
Thursday, 12 March 2009 11:29:59 a.m.

Sample bulk lot ref:
2009023/6

Result Source:
Measurement

Particle Name:
Marine Sediment

Accessory Name:
Hydro 2000G (A)

Analysis model:
General purpose

Sensitivity:
Enhanced

Particle RI:
1.500

Absorption:
0

Size range:
0.020 to 2000.000 um

Obscuration:
19.55 %

Dispersant Name:
Water

Dispersant RI:
1.330

Weighted Residual:
0.690 %

Result Emulation:
Off

Concentration:
0.2362 %Vol

Span :
1.172

Uniformity:
0.38

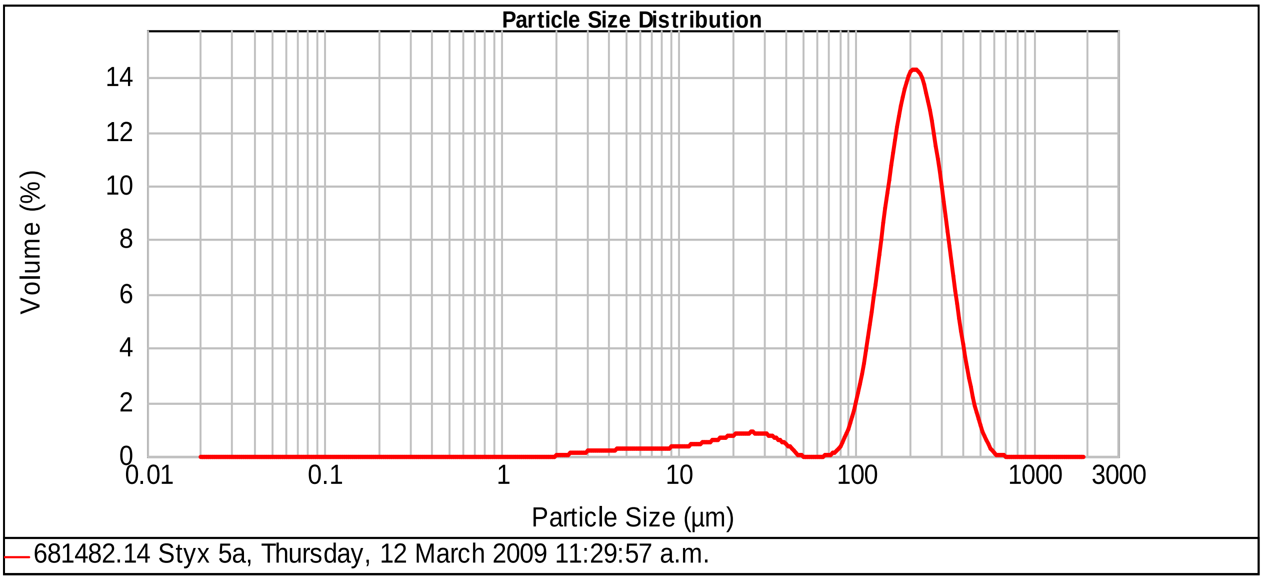
Result units:
Volume

Specific Surface Area:
0.0721 m²/g

Surface Weighted Mean D[3,2]:
83.210 um

Vol. Weighted Mean D[4,3]:
210.811 um

d(0.1): **100.923 um** **d(0.5):** **203.920 um** **d(0.9):** **339.892 um**



Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.050	0.00	0.980	0.00	37.000	0.48	105.000	4.77	300.000	8.46	840.000	0.00
0.060	0.00	2.000	0.53	44.000	0.04	125.000	8.94	350.000	5.77	1000.000	0.00
0.120	0.00	3.900	1.18	53.000	0.00	149.000	12.91	420.000	2.29	2000.000	
0.240	0.00	7.800	1.78	63.000	0.01	177.000	15.51	500.000	0.57		
0.490	0.00	15.600	3.50	74.000	0.41	210.000	16.02	590.000	0.02		
0.700	0.00	31.000	0.81	88.000	1.89	250.000	14.11	710.000	0.00		
0.980		37.000		105.000		300.000		840.000			

Operator notes:

MASTERSIZER 2000

Result Analysis Report

Sample Name:
68148.15 Styx 6

Sample Source & type:

Sample bulk lot ref:
2009023/7

SOP Name:
Marine Sediment

Measured by:
rodgers

Result Source:
Measurement

Measured:
Thursday, 12 March 2009 11:42:58 a.m.

Analysed:
Thursday, 12 March 2009 11:42:59 a.m.

Particle Name:
Marine Sediment

Particle RI:
1.500

Dispersant Name:
Water

Accessory Name:
Hydro 2000G (A)

Absorption:
0

Dispersant RI:
1.330

Analysis model:
General purpose

Size range:
0.020 to 2000.000 um

Weighted Residual:
0.475 %

Sensitivity:
Enhanced

Obscuration:
16.69 %

Result Emulation:
Off

Concentration:
0.0830 %Vol

Specific Surface Area:
0.175 m²/g

Span :
7.747

Surface Weighted Mean D[3,2]:
34.311 um

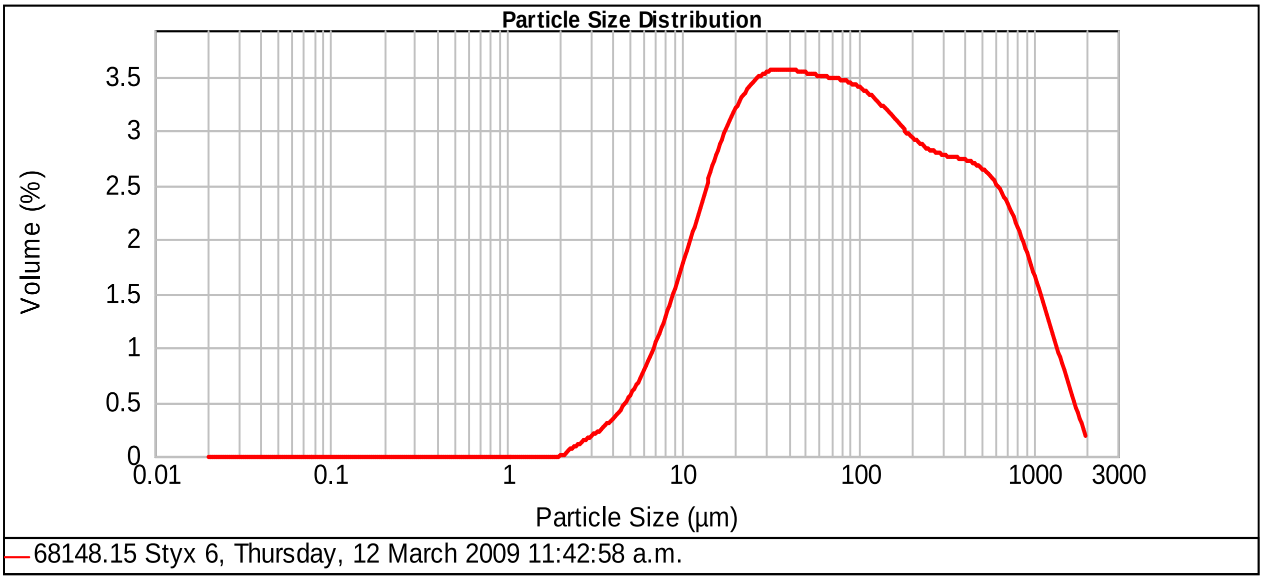
Uniformity:
2.29

Vol. Weighted Mean D[4,3]:
221.213 um

Result units:
Volume

d(0.1): 13.149 um **d(0.5):** 82.145 um **d(0.9):** 649.486 um

---



Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.00
2.000	0.64
3.900	3.19
7.800	9.06
15.600	14.62
31.000	4.12
37.000	

Size (µm)	Volume In %
37.000	4.04
44.000	4.31
53.000	3.97
63.000	3.68
74.000	3.93
88.000	3.95
105.000	

Size (µm)	Volume In %
105.000	3.81
125.000	3.71
149.000	3.49
177.000	3.33
210.000	3.28
250.000	3.35
300.000	

Size (µm)	Volume In %
300.000	2.79
350.000	3.27
420.000	3.08
500.000	2.83
590.000	2.96
710.000	2.41
840.000	

Size (µm)	Volume In %
840.000	2.12
1000.000	4.08
2000.000	

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name:
681482.16 Styx 7

SOP Name:
Marine Sediment

Measured:
Thursday, 12 March 2009 11:57:47 a.m.

Sample Source & type:

Measured by:
rodgers

Analysed:
Thursday, 12 March 2009 11:57:48 a.m.

Sample bulk lot ref:
2009023/8

Result Source:
Measurement

Particle Name:
Marine Sediment

Accessory Name:
Hydro 2000G (A)

Analysis model:
General purpose

Sensitivity:
Enhanced

Particle RI:
1.500

Absorption:
0

Size range:
0.020 to 2000.000 um

Obscuration:
21.26 %

Dispersant Name:
Water

Dispersant RI:
1.330

Weighted Residual:
0.371 %

Result Emulation:
Off

Concentration:
0.1246 %Vol

Span :
5.834

Uniformity:
1.81

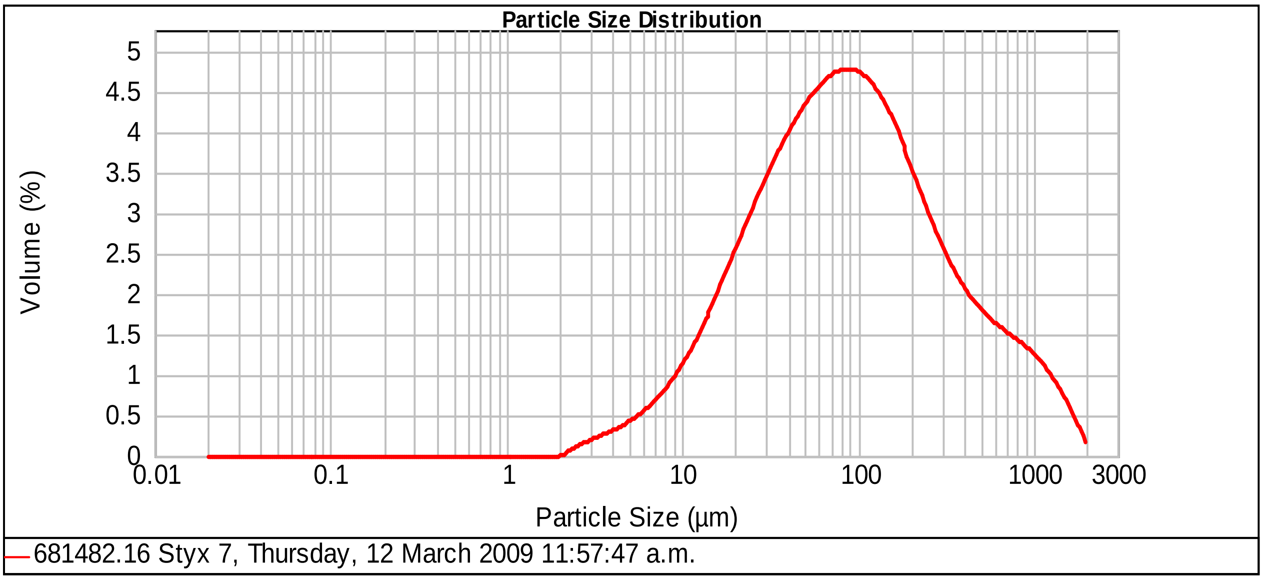
Result units:
Volume

Specific Surface Area:
0.152 m²/g

Surface Weighted Mean D[3,2]:
39.451 um

Vol. Weighted Mean D[4,3]:
194.662 um

d(0.1): 16.765 um **d(0.5): 85.912 um** **d(0.9): 518.008 um**



Size (µm)	Volume In %
0.050	
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	0.00

Size (µm)	Volume In %
0.980	
2.000	0.00
3.900	0.68
7.800	2.32
15.600	6.03
31.000	12.29
37.000	4.25

Size (µm)	Volume In %
37.000	
44.000	4.53
53.000	5.22
63.000	5.11
74.000	4.92
88.000	5.39
105.000	5.49

Size (µm)	Volume In %
105.000	
125.000	5.28
149.000	5.05
177.000	4.58
210.000	4.11
250.000	3.71
300.000	3.37

Size (µm)	Volume In %
300.000	
350.000	2.48
420.000	2.57
500.000	2.18
590.000	1.87
710.000	1.92
840.000	1.61

Size (µm)	Volume In %
840.000	
1000.000	1.52
2000.000	3.49

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name:
682318.17 Ee5 Plot 4-6 (composite)

SOP Name:
Marine Sediment

Measured:
Wednesday, 11 March 2009 10:39:27 a.m.

Sample Source & type:

Measured by:
rodgers

Analysed:
Wednesday, 11 March 2009 10:39:29 a.m.

Sample bulk lot ref:
2009025/2

Result Source:
Measurement

Particle Name:
Marine Sediment

Accessory Name:
Hydro 2000G (A)

Analysis model:
General purpose

Sensitivity:
Enhanced

Particle RI:
1.500

Absorption:
0

Size range:
0.020 to 2000.000 um

Obscuration:
14.76 %

Dispersant Name:
Water

Dispersant RI:
1.330

Weighted Residual:
0.632 %

Result Emulation:
Off

Concentration:
0.1240 %Vol

Span :
1.109

Uniformity:
0.355

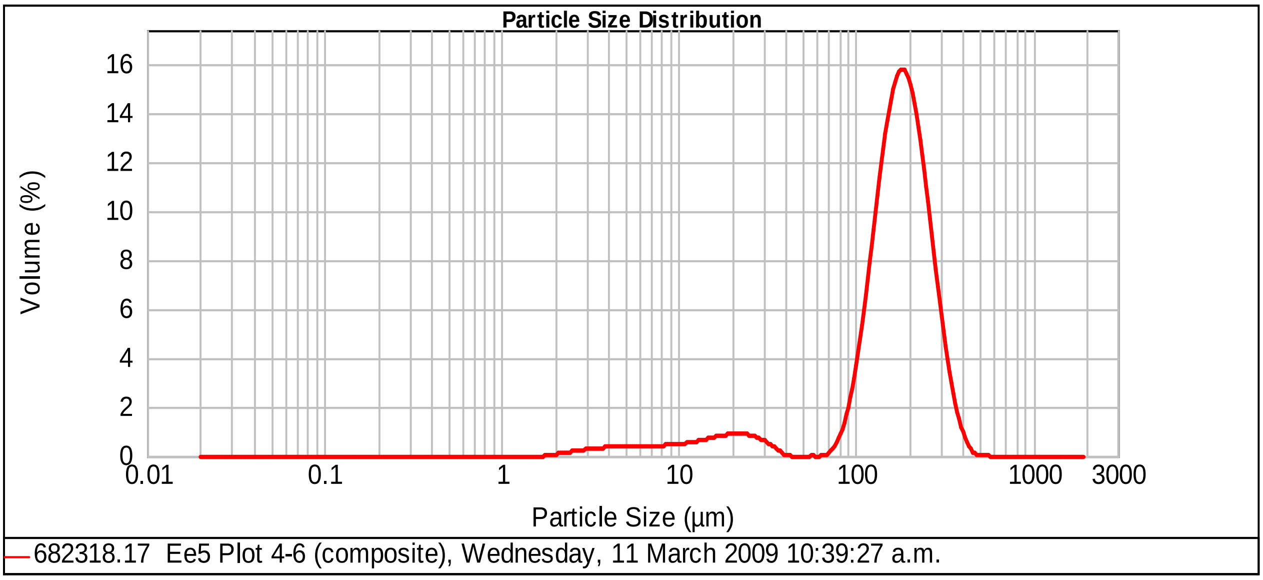
Result units:
Volume

Specific Surface Area:
0.0972 m²/g

Surface Weighted Mean D[3,2]:
61.748 um

Vol. Weighted Mean D[4,3]:
174.231 um

d(0.1): 82.066 um **d(0.5): 172.773 um** **d(0.9): 273.614 um**



Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.02
2.000	1.00
3.900	1.80
7.800	2.50
15.600	3.70
31.000	0.44
37.000	

Size (µm)	Volume In %
37.000	0.05
44.000	0.00
53.000	-0.00
63.000	0.10
74.000	0.97
88.000	3.57
105.000	

Size (µm)	Volume In %
105.000	7.99
125.000	13.39
149.000	16.97
177.000	17.35
210.000	14.59
250.000	9.73
300.000	

Size (µm)	Volume In %
300.000	4.04
350.000	1.62
420.000	0.16
500.000	0.00
590.000	0.00
710.000	0.00
840.000	

Size (µm)	Volume In %
840.000	0.00
1000.000	0.00
2000.000	

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name:
681482.18 Styx 9a

SOP Name:
Marine Sediment

Measured:
Thursday, 12 March 2009 2:00:07 p.m.

Sample Source & type:

Measured by:
rodgers

Analysed:
Thursday, 12 March 2009 2:00:08 p.m.

Sample bulk lot ref:
2009023/10

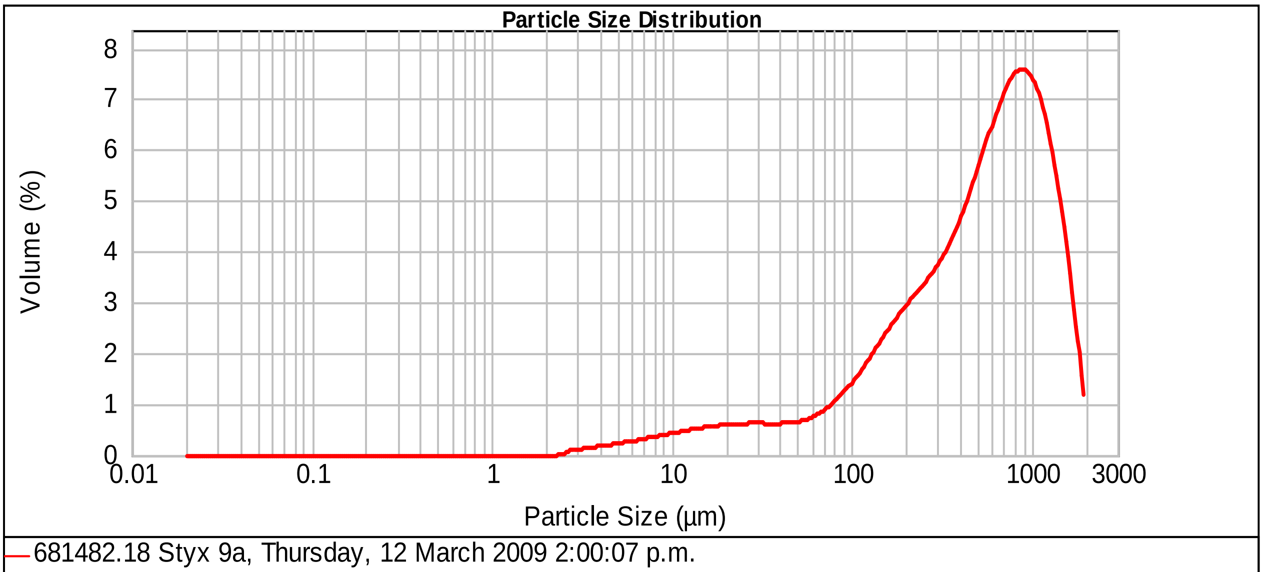
Result Source:
Measurement

Particle Name: Marine Sediment	**Accessory Name:** Hydro 2000G (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 1.500	**Absorption:** 0	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 12.53 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 0.773 %	**Result Emulation:** Off

---

Concentration: 0.1883 %Vol	**Span :** 2.256	**Uniformity:** 0.699	**Result units:** Volume
Specific Surface Area: 0.0563 m²/g	**Surface Weighted Mean D[3,2]:** 106.555 um	**Vol. Weighted Mean D[4,3]:** 627.000 um	

d(0.1): 71.560 um **d(0.5): 549.690 um** **d(0.9): 1311.733 um**



Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.00
2.000	0.35
3.900	1.16
7.800	2.06
15.600	2.72
31.000	0.72
37.000	

Size (µm)	Volume In %
37.000	0.71
44.000	0.79
53.000	0.81
63.000	0.89
74.000	1.19
88.000	1.56
105.000	

Size (µm)	Volume In %
105.000	1.96
125.000	2.44
149.000	2.84
177.000	3.21
210.000	3.64
250.000	4.21
300.000	

Size (µm)	Volume In %
300.000	3.95
350.000	5.30
420.000	5.91
500.000	6.49
590.000	8.26
710.000	8.17
840.000	

Size (µm)	Volume In %
840.000	8.62
1000.000	22.06
2000.000	

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name:
682318.19 Ee5 Plot 10-12 (composite)

SOP Name:
Marine Sediment

Measured:
Wednesday, 11 March 2009 11:02:37 a.m.

Sample Source & type:

Measured by:
rodgers

Analysed:
Wednesday, 11 March 2009 11:02:39 a.m.

Sample bulk lot ref:
2009025/4

Result Source:
Measurement

Particle Name:
Marine Sediment

Accessory Name:
Hydro 2000G (A)

Analysis model:
General purpose

Sensitivity:
Enhanced

Particle RI:
1.500

Absorption:
0

Size range:
0.020 to 2000.000 um

Obscuration:
18.30 %

Dispersant Name:
Water

Dispersant RI:
1.330

Weighted Residual:
0.620 %

Result Emulation:
Off

Concentration:
0.1799 %Vol

Span :
1.021

Uniformity:
0.339

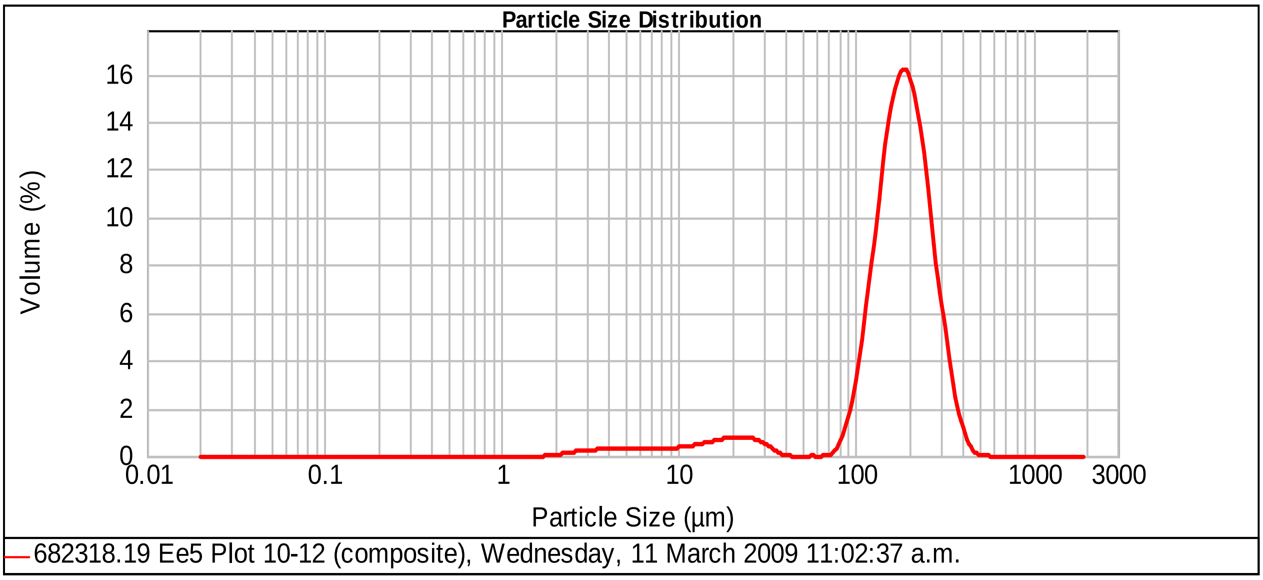
Result units:
Volume

Specific Surface Area:
0.085 m²/g

Surface Weighted Mean D[3,2]:
70.554 um

Vol. Weighted Mean D[4,3]:
181.499 um

d(0.1): 98.329 um **d(0.5): 178.546 um** **d(0.9): 280.607 um**



Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.050	0.00	0.980	0.02	37.000	0.02	105.000	7.60	300.000	4.80	840.000	0.00
0.060	0.00	2.000	0.86	44.000	0.00	125.000	12.85	350.000	1.91	1000.000	0.00
0.120	0.00	3.900	1.41	53.000	0.00	149.000	17.11	420.000	0.24	2000.000	
0.240	0.00	7.800	1.92	63.000	0.03	177.000	17.95	500.000	0.01		
0.490	0.00	15.600	3.22	74.000	0.71	210.000	15.58	590.000	0.00		
0.700	0.00	31.000	0.32	88.000	3.02	250.000	10.44	710.000	0.00		
0.980		37.000		105.000		300.000		840.000			

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name:
681482.20 Styx11

SOP Name:
Marine Sediment

Measured:
Friday, 13 March 2009 9:20:12 a.m.

Sample Source & type:

Measured by:
rodgers

Analysed:
Friday, 13 March 2009 9:20:13 a.m.

Sample bulk lot ref:
2009023/12

Result Source:
Measurement

Particle Name:
Marine Sediment

Accessory Name:
Hydro 2000G (A)

Analysis model:
General purpose

Sensitivity:
Enhanced

Particle RI:
1.500

Absorption:
0

Size range:
0.020 to 2000.000 um

Obscuration:
21.23 %

Dispersant Name:
Water

Dispersant RI:
1.330

Weighted Residual:
0.526 %

Result Emulation:
Off

Concentration:
0.0617 %Vol

Span :
7.414

Uniformity:
2.6

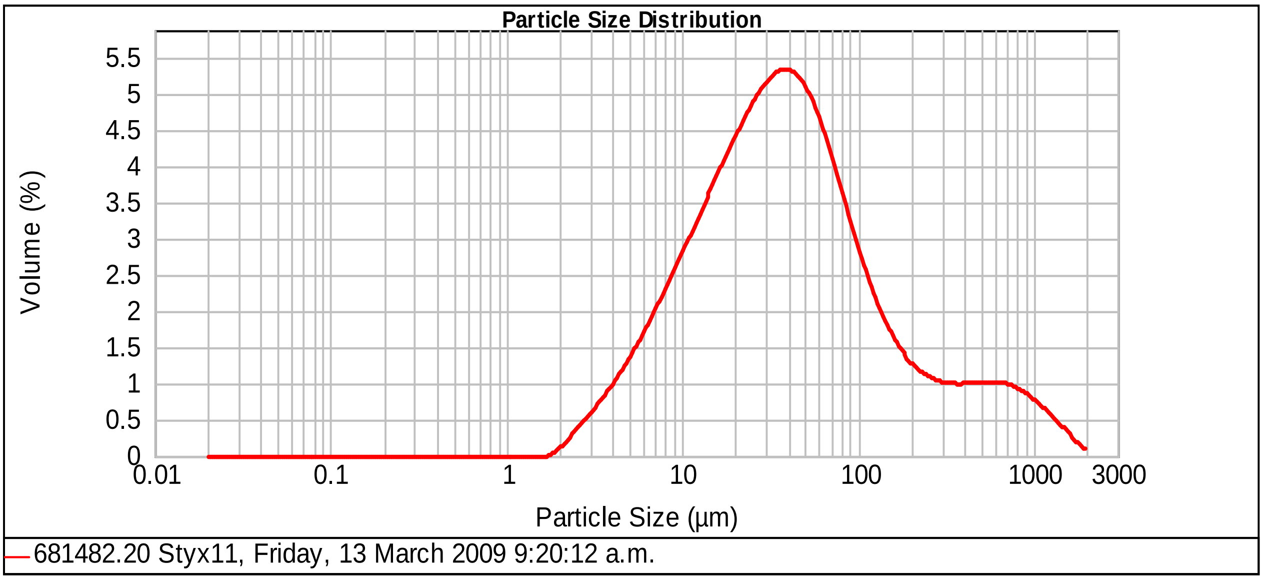
Result units:
Volume

Specific Surface Area:
0.297 m²/g

Surface Weighted Mean D[3,2]:
20.199 um

Vol. Weighted Mean D[4,3]:
115.074 um

d(0.1): 8.184 um **d(0.5): 37.359 um** **d(0.9): 285.156 um**



Size (µm)	Volume In %
0.050	
	0.00
0.060	
	0.00
0.120	
	0.00
0.240	
	0.00
0.490	
	0.00
0.700	
	0.00
0.980	

Size (µm)	Volume In %
0.980	
	0.03
2.000	
	2.18
3.900	
	7.06
7.800	
	13.80
15.600	
	20.48
31.000	
	6.11
37.000	

Size (µm)	Volume In %
37.000	
	6.04
44.000	
	6.28
53.000	
	5.39
63.000	
	4.47
74.000	
	4.13
88.000	
	3.47
105.000	

Size (µm)	Volume In %
105.000	
	2.77
125.000	
	2.24
149.000	
	1.79
177.000	
	1.50
210.000	
	1.33
250.000	
	1.27
300.000	

Size (µm)	Volume In %
300.000	
	1.02
350.000	
	1.19
420.000	
	1.15
500.000	
	1.11
590.000	
	1.23
710.000	
	1.06
840.000	

Size (µm)	Volume In %
840.000	
	0.97
1000.000	
	1.93
2000.000	

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name:
681482.21 Styx 12

SOP Name:
Marine Sediment

Measured:
Friday, 13 March 2009 9:32:41 a.m.

Sample Source & type:

Measured by:
rodgers

Analysed:
Friday, 13 March 2009 9:32:42 a.m.

Sample bulk lot ref:
2009023/13

Result Source:
Measurement

Particle Name:
Marine Sediment

Accessory Name:
Hydro 2000G (A)

Analysis model:
General purpose

Sensitivity:
Enhanced

Particle RI:
1.500

Absorption:
0

Size range:
0.020 to 2000.000 um

Obscuration:
21.19 %

Dispersant Name:
Water

Dispersant RI:
1.330

Weighted Residual:
0.361 %

Result Emulation:
Off

Concentration:
0.1196 %Vol

Span :
4.945

Uniformity:
1.67

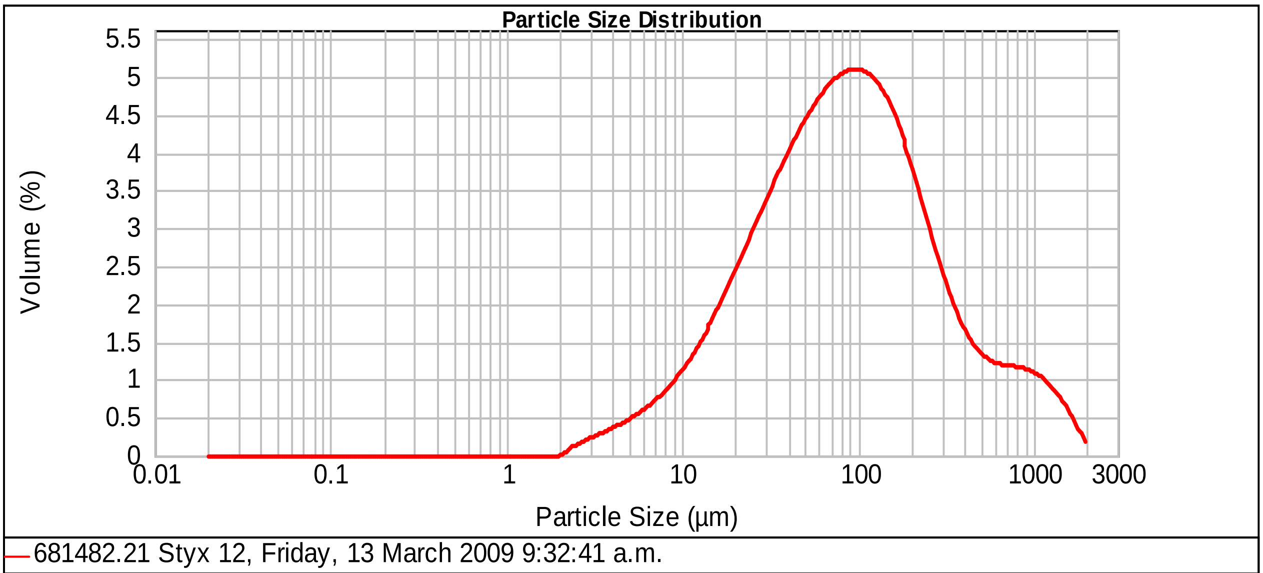
Result units:
Volume

Specific Surface Area:
0.157 m²/g

Surface Weighted Mean D[3,2]:
38.208 um

Vol. Weighted Mean D[4,3]:
180.036 um

d(0.1): 16.499 um **d(0.5): 84.364 um** **d(0.9): 433.694 um**



Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.00
2.000	0.81
3.900	2.54
7.800	5.93
15.600	11.89
31.000	4.21
37.000	

Size (µm)	Volume In %
37.000	4.55
44.000	5.32
53.000	5.28
63.000	5.15
74.000	5.71
88.000	5.89
105.000	

Size (µm)	Volume In %
105.000	5.74
125.000	5.54
149.000	5.03
177.000	4.46
210.000	3.89
250.000	3.32
300.000	

Size (µm)	Volume In %
300.000	2.26
350.000	2.14
420.000	1.67
500.000	1.39
590.000	1.46
710.000	1.30
840.000	

Size (µm)	Volume In %
840.000	1.30
1000.000	3.21
2000.000	

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name:
681482.1 Styx 14

SOP Name:
Marine Sediment

Measured:
Wednesday, 8 April 2009 8:03:53 a.m.

Sample Source & type:

Measured by:
jacinta

Analysed:
Wednesday, 8 April 2009 8:03:54 a.m.

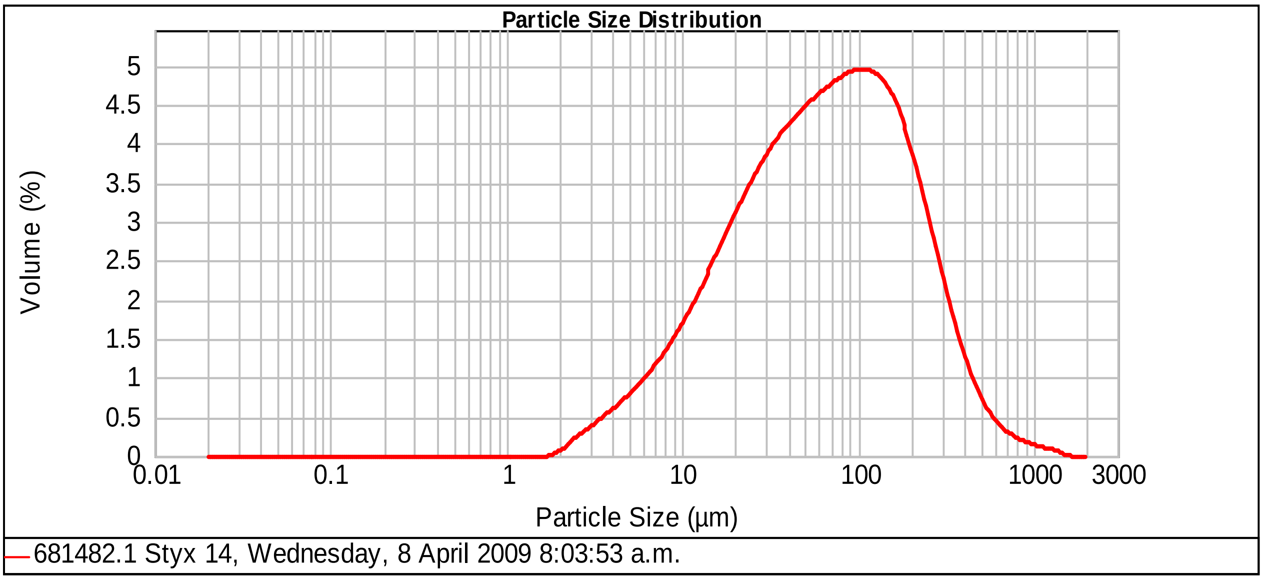
Sample bulk lot ref:
2009039-1

Result Source:
Measurement

Particle Name:	**Accessory Name:**	**Analysis model:**	**Sensitivity:**
Marine Sediment	Hydro 2000G (A)	General purpose	Enhanced
Particle RI:	**Absorption:**	**Size range:**	**Obscuration:**
1.500	0	0.020 to 2000.000 um	13.77 %
Dispersant Name:	**Dispersant RI:**	**Weighted Residual:**	**Result Emulation:**
Water	1.330	0.522 %	Off

Concentration:	**Span :**	**Uniformity:**	**Result units:**
0.0548 %Vol	3.668	1.21	Volume
Specific Surface Area:	**Surface Weighted Mean D[3,2]:**	**Vol. Weighted Mean D[4,3]:**	
0.209 m²/g	28.663 um	108.234 um	

d(0.1): 11.790 um **d(0.5):** 65.240 um **d(0.9):** 251.073 um



Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.02
2.000	1.39
3.900	4.13
7.800	8.63
15.600	14.66
31.000	4.66
37.000	

Size (µm)	Volume In %
37.000	4.82
44.000	5.41
53.000	5.21
63.000	4.99
74.000	5.51
88.000	5.71
105.000	

Size (µm)	Volume In %
105.000	5.63
125.000	5.53
149.000	5.10
177.000	4.56
210.000	3.96
250.000	3.29
300.000	

Size (µm)	Volume In %
300.000	2.10
350.000	1.75
420.000	1.09
500.000	0.66
590.000	0.47
710.000	0.28
840.000	

Size (µm)	Volume In %
840.000	0.20
1000.000	0.24
2000.000	

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name:
681482.2 Styx 15

SOP Name:
Marine Sediment

Measured:
Wednesday, 8 April 2009 8:14:46 a.m.

Sample Source & type:

Measured by:
jacinta

Analysed:
Wednesday, 8 April 2009 8:14:47 a.m.

Sample bulk lot ref:
2009039-2

Result Source:
Measurement

Particle Name:
Marine Sediment

Accessory Name:
Hydro 2000G (A)

Analysis model:
General purpose

Sensitivity:
Enhanced

Particle RI:
1.500

Absorption:
0

Size range:
0.020 to 2000.000 um

Obscuration:
15.01 %

Dispersant Name:
Water

Dispersant RI:
1.330

Weighted Residual:
0.653 %

Result Emulation:
Off

Concentration:
0.0673 %Vol

Span :
6.416

Uniformity:
1.96

Result units:
Volume

Specific Surface Area:
0.19 m²/g

Surface Weighted Mean D[3,2]:
31.625 um

Vol. Weighted Mean D[4,3]:
169.206 um

d(0.1): 12.763 um **d(0.5):** 70.493 um **d(0.9):** 465.014 um

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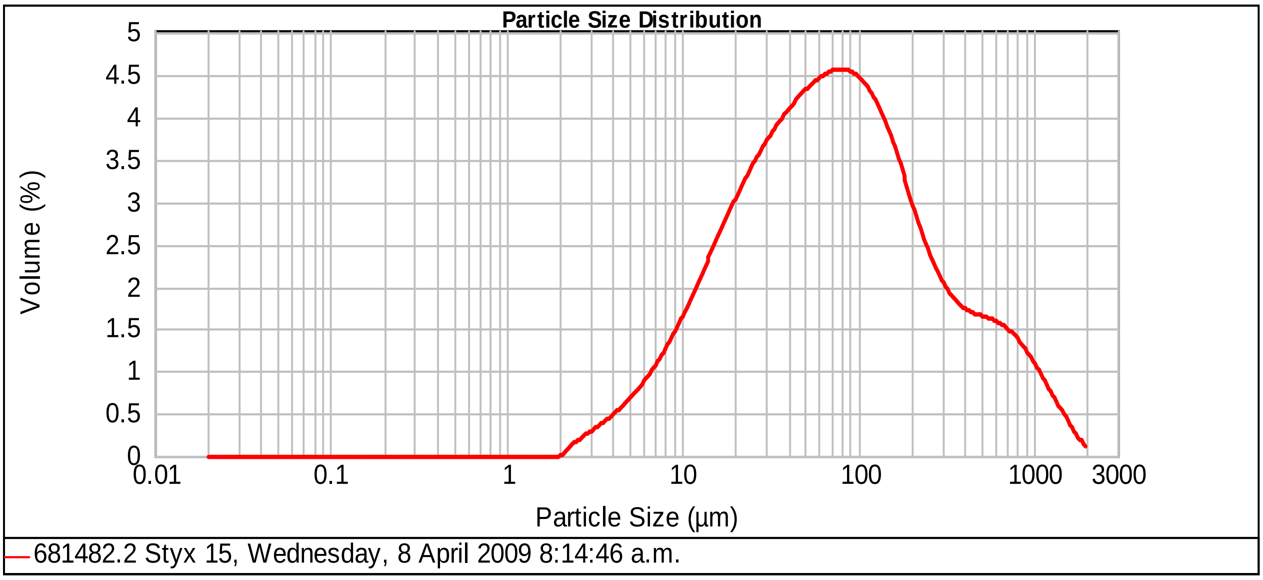


Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.00
2.000	1.02
3.900	3.63
7.800	8.41
15.600	14.26
31.000	4.48
37.000	

Size (µm)	Volume In %
37.000	4.64
44.000	5.22
53.000	5.02
63.000	4.78
74.000	5.18
88.000	5.21
105.000	

Size (µm)	Volume In %
105.000	4.94
125.000	4.62
149.000	4.08
177.000	3.53
210.000	3.06
250.000	2.70
300.000	

Size (µm)	Volume In %
300.000	1.98
350.000	2.13
420.000	1.92
500.000	1.77
590.000	1.89
710.000	1.57
840.000	

Size (µm)	Volume In %
840.000	1.40
1000.000	2.58
2000.000	

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

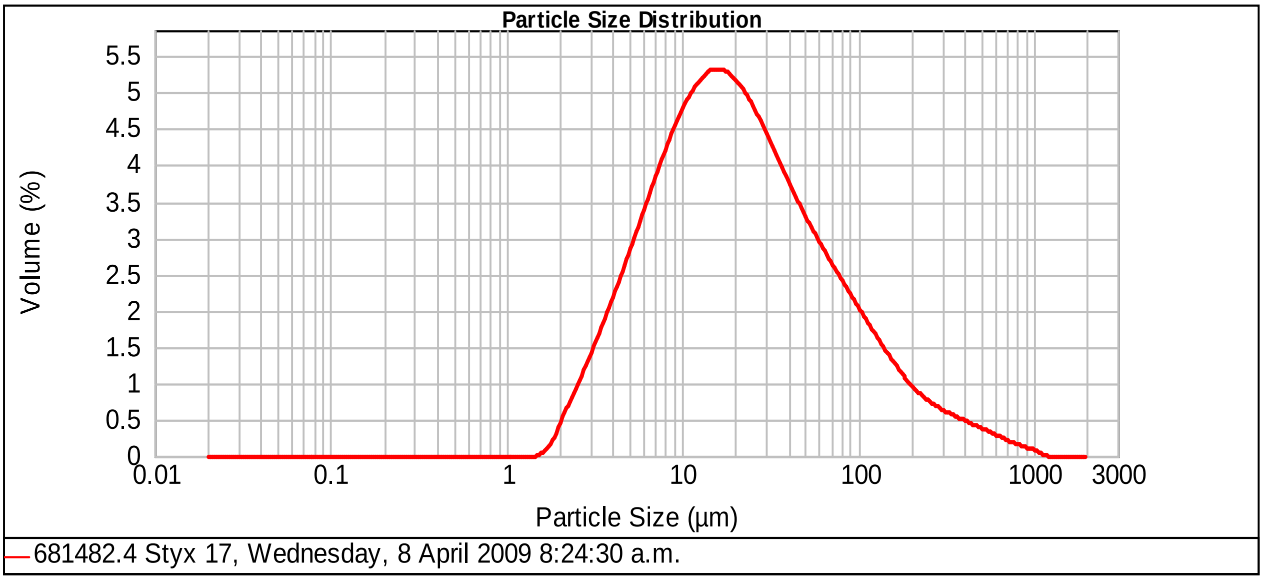
Result Analysis Report

Sample Name: 681482.4 Styx 17	**SOP Name:** Marine Sediment	**Measured:** Wednesday, 8 April 2009 8:24:30 a.m.
Sample Source & type:	**Measured by:** jacinta	**Analysed:** Wednesday, 8 April 2009 8:24:31 a.m.
Sample bulk lot ref: 2009039-3	**Result Source:** Measurement	

Particle Name: Marine Sediment	**Accessory Name:** Hydro 2000G (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 1.500	**Absorption:** 0	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 14.00 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 0.545 %	**Result Emulation:** Off

Concentration: 0.0229 %Vol	**Span :** 5.497	**Uniformity:** 2.03	**Result units:** Volume
Specific Surface Area: 0.485 m²/g	**Surface Weighted Mean D[3,2]:** 12.366 um	**Vol. Weighted Mean D[4,3]:** 49.959 um	

d(0.1): 5.120 um **d(0.5): 19.706 um** **d(0.9): 113.451 um**



Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.26
2.000	5.33
3.900	14.11
7.800	22.22
15.600	22.44
31.000	4.84
37.000	

Size (µm)	Volume In %
37.000	4.28
44.000	4.12
53.000	3.42
63.000	2.85
74.000	2.74
88.000	2.44
105.000	

Size (µm)	Volume In %
105.000	2.07
125.000	1.75
149.000	1.41
177.000	1.15
210.000	0.97
250.000	0.84
300.000	

Size (µm)	Volume In %
300.000	0.61
350.000	0.62
420.000	0.49
500.000	0.38
590.000	0.32
710.000	0.20
840.000	

Size (µm)	Volume In %
840.000	0.13
1000.000	0.04
2000.000	

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

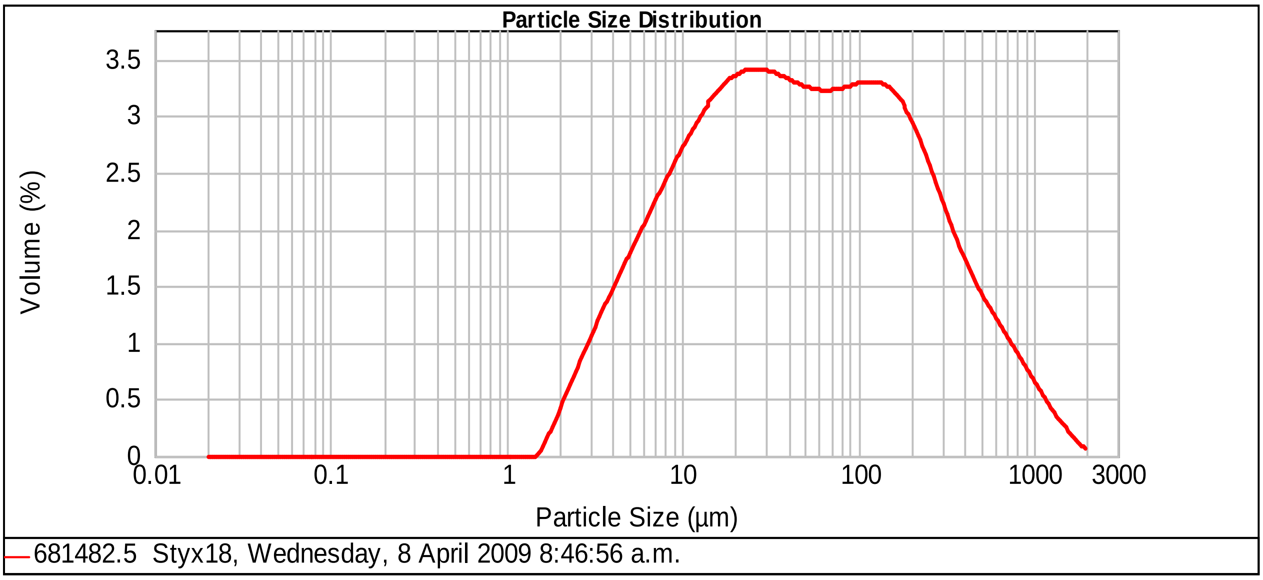
Result Analysis Report

Sample Name: 681482.5 Styx18	**SOP Name:** Marine Sediment	**Measured:** Wednesday, 8 April 2009 8:46:56 a.m.
Sample Source & type:	**Measured by:** jacinta	**Analysed:** Wednesday, 8 April 2009 8:46:57 a.m.
Sample bulk lot ref: 2009039-4	**Result Source:** Measurement	

Particle Name: Marine Sediment	**Accessory Name:** Hydro 2000G (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 1.500	**Absorption:** 0	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 14.69 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 0.463 %	**Result Emulation:** Off

Concentration: 0.0343 %Vol	**Span :** 7.420	**Uniformity:** 2.46	**Result units:** Volume
Specific Surface Area: 0.337 m²/g	**Surface Weighted Mean D[3,2]:** 17.815 um	**Vol. Weighted Mean D[4,3]:** 133.485 um	

d(0.1): 6.354 um **d(0.5): 46.975 um** **d(0.9): 354.889 um**



Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.31
2.000	4.03
3.900	8.69
7.800	12.82
15.600	15.07
31.000	3.91
37.000	

Size (µm)	Volume In %
37.000	3.77
44.000	3.98
53.000	3.65
63.000	3.39
74.000	3.68
88.000	3.79
105.000	

Size (µm)	Volume In %
105.000	3.76
125.000	3.77
149.000	3.60
177.000	3.38
210.000	3.16
250.000	2.92
300.000	

Size (µm)	Volume In %
300.000	2.15
350.000	2.19
420.000	1.78
500.000	1.46
590.000	1.39
710.000	1.05
840.000	

Size (µm)	Volume In %
840.000	0.87
1000.000	1.45
2000.000	

Operator notes:

MASTERSIZER 2000

Result Analysis Report

Sample Name:
681482.7 Styx 20

Sample Source & type:

Sample bulk lot ref:
2009039-5

SOP Name:
Marine Sediment

Measured by:
jacinta

Result Source:
Measurement

Measured:
Wednesday, 8 April 2009 8:56:57 a.m.

Analysed:
Wednesday, 8 April 2009 8:56:59 a.m.

Particle Name:
Marine Sediment

Particle RI:
1.500

Dispersant Name:
Water

Accessory Name:
Hydro 2000G (A)

Absorption:
0

Dispersant RI:
1.330

Analysis model:
General purpose

Size range:
0.020 to 2000.000 um

Weighted Residual:
0.519 %

Sensitivity:
Enhanced

Obscuration:
15.02 %

Result Emulation:
Off

Concentration:
0.0392 %Vol

Specific Surface Area:
0.311 m²/g

Span :
5.276

Surface Weighted Mean D[3,2]:
19.274 um

Uniformity:
1.63

Vol. Weighted Mean D[4,3]:
88.288 um

Result units:
Volume

d(0.1): 7.302 um   **d(0.5):** 43.088 um   **d(0.9):** 234.642 um

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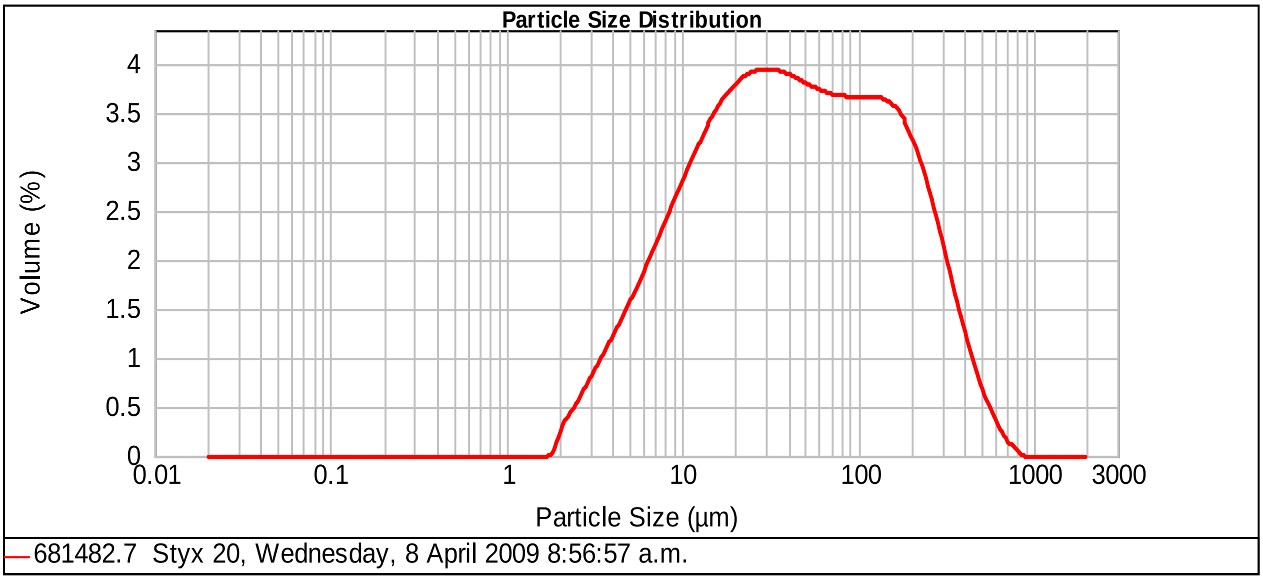


Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.05
2.000	3.05
3.900	7.89
7.800	13.48
15.600	17.11
31.000	4.55
37.000	

Size (µm)	Volume In %
37.000	4.40
44.000	4.65
53.000	4.24
63.000	3.89
74.000	4.16
88.000	4.23
105.000	

Size (µm)	Volume In %
105.000	4.17
125.000	4.18
149.000	3.99
177.000	3.74
210.000	3.42
250.000	3.00
300.000	

Size (µm)	Volume In %
300.000	2.00
350.000	1.72
420.000	1.07
500.000	0.60
590.000	0.33
710.000	0.09
840.000	

Size (µm)	Volume In %
840.000	0.00
1000.000	0.00
2000.000	

Operator notes:

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name:
681482.22 Styx 13

SOP Name:
Marine Sediment

Measured:
Wednesday, 8 April 2009 9:11:12 a.m.

Sample Source & type:

Measured by:
jacinta

Analysed:
Wednesday, 8 April 2009 9:11:13 a.m.

Sample bulk lot ref:
2009039-6

Result Source:
Measurement

Particle Name:
Marine Sediment

Accessory Name:
Hydro 2000G (A)

Analysis model:
General purpose

Sensitivity:
Enhanced

Particle RI:
1.500

Absorption:
0

Size range:
0.020 to 2000.000 um

Obscuration:
14.69 %

Dispersant Name:
Water

Dispersant RI:
1.330

Weighted Residual:
0.536 %

Result Emulation:
Off

Concentration:
0.0544 %Vol

Span :
4.674

Uniformity:
1.6

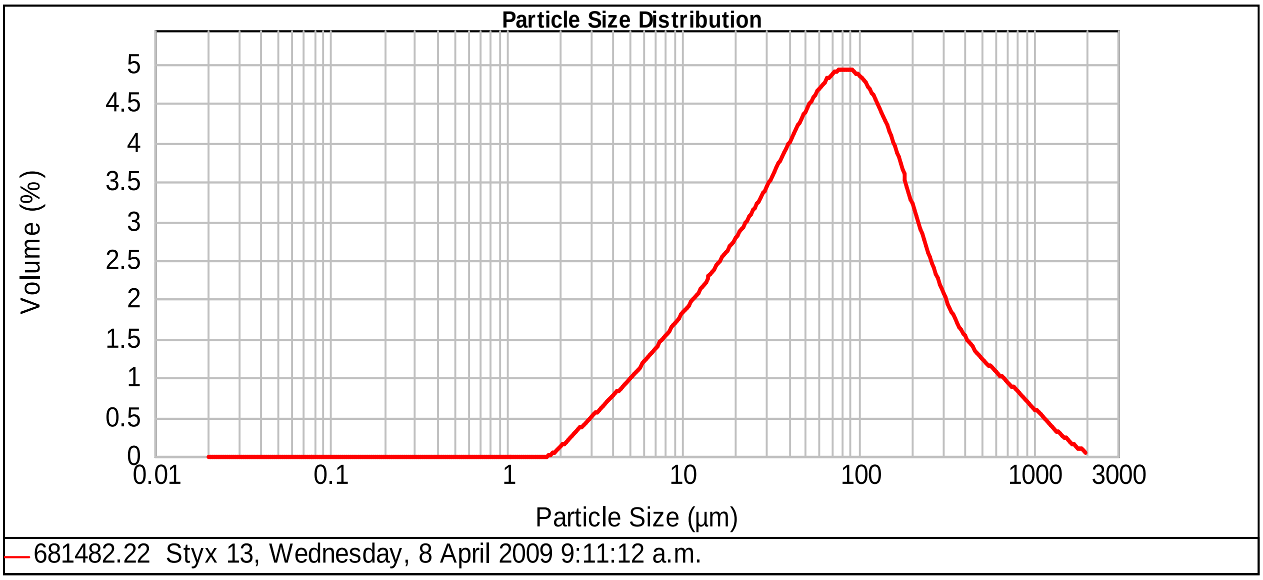
Result units:
Volume

Specific Surface Area:
0.223 m²/g

Surface Weighted Mean D[3,2]:
26.919 um

Vol. Weighted Mean D[4,3]:
136.826 um

d(0.1): 10.390 um **d(0.5): 67.259 um** **d(0.9): 324.733 um**



Size (µm)	Volume In %
0.050	0.00
0.060	0.00
0.120	0.00
0.240	0.00
0.490	0.00
0.700	0.00
0.980	

Size (µm)	Volume In %
0.980	0.03
2.000	1.80
3.900	5.00
7.800	8.85
15.600	13.07
31.000	4.21
37.000	

Size (µm)	Volume In %
37.000	4.51
44.000	5.26
53.000	5.23
63.000	5.08
74.000	5.58
88.000	5.64
105.000	

Size (µm)	Volume In %
105.000	5.35
125.000	5.00
149.000	4.40
177.000	3.81
210.000	3.29
250.000	2.83
300.000	

Size (µm)	Volume In %
300.000	1.98
350.000	1.94
420.000	1.56
500.000	1.28
590.000	1.24
710.000	0.95
840.000	

Size (µm)	Volume In %
840.000	0.80
1000.000	1.32
2000.000	

Operator notes:

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