

Contaminants in Hamilton's urban stream sediments and ecotoxicity to amphipods

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Executive summary

NIWA was commissioned by the Waikato Regional Council to survey contaminants in urban stream sediments in Hamilton and determine if sediment-associated contaminants are likely to inhibit restoration of these waterways. The focus of the present study was on sediment-associated contaminants. Dissolved or waterborne contaminant concentrations were not evaluated, however dissolved contaminants can significantly impact urban streams.

In June 2011 sediments were sampled at 27 locations in streams in the city of Hamilton and in May 2012 a subset of these locations was sampled again. Sediments at almost all locations were primarily sandy with some fines. Up to 23 elements were measured in the <500 µm sediments in both years, and in 2012 organochlorine (OC) and polycyclic aromatic hydrocarbon (PAH) concentrations were also measured. In 2012 the sediments were also evaluated in a 10 day amphipod toxicity test and fine fraction (<63 µm) sediments were analysed for multiple elements.

Concentrations of up to 23 elements in stream sediments were compared:

1. across locations in the present study to establish an expected range, and sites $\geq 3x$ median concentrations were designated as outliers
2. to ANZECC (2000) Interim Sediment Quality Guidelines (ISQG), and
3. to a recent Waikato survey of terrestrial soils (Taylor et al. 2010).

Findings:

Zinc accumulation

- Median zinc (Zn) concentrations in the present study were 67 to 147 mg kg⁻¹ dwt in the <500 µm sediment fraction (range 20 to 1539 mg kg⁻¹ dwt), compared to 28 mg kg⁻¹ dwt in background soils (range 11 to 58). Our data supports the suggestion by Kim (2011) that Zn is accumulating in aquatic sediments from urban stormwater and use as a facial eczema remedy for agricultural stock.

Mangakotukutuku Stream

- Contaminant concentrations in the Rukuhia and Te Anau branches of the Mangakotukutuku Stream were low suggesting the combination of rural inputs to the upper Rukuhia and Te Anau with established urban inputs to the lower sections of these catchments has resulted in minimal detectable contamination of the sediments in this waterway. Amphipod survival was 95% in Rukuhia sediments.
- Contaminant signatures in the Peacockes branch of the Mangakotukutuku suggest that fertilizer application, agricultural supplements, or historic land use has resulted in some accumulation of contaminants in stream sediments. Amphipod survival was 88% to 93% in Peacockes sediments indicating sediment-associated contaminant bioavailability and toxicity is low.

Waitawhiriwhiri Stream

- The limited sampling conducted on the Waitawhiriwhiri catchment suggested that apart from Rotoroa Lake (Waitawhiriwhiri A), and Waitawhiriwhiri E (where lead (Pb) was 3x median concentrations) contaminant concentrations were relatively low in stream sediments in this catchment. Sediments in this catchment were not analysed for OCs or PAHs except at Rotoroa Lake and amphipods were only exposed to sediments from Rotoroa Lake, limiting the inferences that can be made about the effects of sediment contaminants in this catchment. Amphipod survival was significantly lower (67%) in Lake Rotoroa sediments compared to control sediments.

Kirikiroa Stream

- The combination of large amounts of iron (Fe) floc and high concentrations of Zn may have decreased survival of amphipods in the muddy sediments from Kirikiroa A (a rural location). Arsenic (As) exceeded ANZECC (2000) ISQG-Low (ISQG-L) lower in the catchment, and was 3x median concentrations at two locations but amphipod survival rates were high in these sediments. Our data suggest that contaminant bioavailability and toxicity is generally low in stream sediments in this catchment.

Bankwood Park

- Compared to other locations investigated in this study, contaminant concentrations in Bankwood stream sediments were relatively low with the exception of Zn and Pb which were 3x median concentrations. Zinc and As exceeded ANZECC ISQG-L but amphipod survival rates were high suggesting that sediment-associated contaminant bioavailability and toxicity is low in this waterway.

Normandy Ave, Graham and Parana Parks, Ranfurly Stream

- At Normandy A, Graham A, Parana A, Ranfurly A and Ranfurly B a wide range of contaminants was present at $\geq 3x$ median concentrations in the present study, suggesting that either historic or current contamination sources affect these waterways. Amphipod survival was greater than 90% in sediments from all of these locations except Normandy A. It is likely then, with the exception of Normandy A, that contaminant bioavailability and toxicity associated with the sediments at these locations is relatively low.
- The results of the amphipod toxicity test indicate that sediment-associated contaminants at Normandy A could have some slight inhibitory effects on stream fauna.

Amphipod toxicity test results

- The results of the amphipod test suggest that although the sediments at some locations in Hamilton's urban streams are contaminated with a range of elements above background concentrations in the region, their bioavailability and toxicity to aquatic biota are relatively low. Waitawhiriwhiri A is an exception

to this, probably primarily due to the legacy of the sodium arsenite application to Rotoroa Lake for aquatic plant control in the 1950's, and significant contamination from urban runoff as demonstrated by previous studies.

- Amphipod survival was <90% at: Kirikiriroa A, a rural stream affected by fertilizer application, iron floc and sedimentation; Normandy A an urban stream affected by a chemical spill in 2002 and possibly also historic land use upstream, and; Peacockes D a rural stream in a catchment affected by agricultural application of fertilizer, stock supplements, and possibly historic horticultural activities.

Recommendations for future evaluation of contaminants

- The most contaminated sites in the present study could have been identified by Zn, Pb, or As concentrations in the sediments that exceeded the ISQG-L guidelines in the <63 μm fraction. Evaluating contaminant concentrations in the <500 μm sediments would not have identified Normandy A or Kirikiriroa A as locations with contaminant concentrations above median values in the present study. In future surveys of urban contaminants in Hamilton we therefore recommend that sediments are analysed for Zn, Pb, Cu, and As in the <63 μm fraction. Many urban locations in Hamilton are potentially influenced by agricultural activity upstream therefore more thorough investigations could include cadmium in the initial suite of contaminants as this may reveal legacy contamination or significant on-going agricultural contaminant inputs.

1 Introduction

1.1 Background

Multiple factors are known to affect urban streams reducing both biodiversity and abundance of aquatic biota (Meyer et al. 2005, Walsh et al. 2005). Changes to urban streams include alteration of flow regimes, channelization (and “burying” of streams), loss of riparian cover, loss of fish and invertebrate passage up- and downstream, reduction of instream habitat complexity and diversity, and an increase in contaminants in water and sediments.

Degradation of urban streams is strongly linked to an increase in impervious surface area in the catchment that changes flow regimes in a characteristic manner. The suite of characteristics typical of urban streams is known as the “urban stream syndrome” (Meyer et al. 2005). Urban streams in Hamilton exhibit many of these characteristics, with decreased invertebrate and vertebrate biodiversity relative to streams in native forest (Collier et al. 2009, Collier et al. 2008). Some urban streams in Hamilton have, however, remnant populations of native fish and invertebrates that can potentially be retained or enhanced through strategic management (Collier et al. 2008). Multiple urban stream and gully restoration projects are underway in Hamilton. Limited resources are available to support these projects many of which are organised by volunteers, therefore it is important to focus restoration work in a cost-effective manner.

There is some concern that contaminants could limit the results of restoration efforts in Hamilton. Contaminants can be present as a legacy of past land-use (e.g., landfill leachate, industrial practices) or from on-going inputs (e.g., urban road-run off, metal-contaminated stormwater). A previous study in Hamilton streams demonstrated that during storm events dissolved zinc (Zn) and copper (Cu) concentrations exceed water quality guidelines and are accompanied by increased loads of faecal coliforms and *Escherichia coli* (Hickey et al. 2001). Although Zn and Cu are commonly associated with urban road and roof stormwater, it is thought that in Hamilton rural use of 5090 to 8500 tonnes/yr Zn in agricultural supplements to combat facial eczema in stock is contributing significant loads to both urban and rural waterways (Kim 2011). To our knowledge there are no other recent studies available on contaminant concentrations in the sediments of Hamilton waterways, apart from studies of Lake Rotoroa investigating the legacy of sodium arsenate application in 1957 to control pest aquatic plants (Rumsby 2008, Tanner & Clayton 1990). Waikato Regional Council has recently completed a multi-element analysis of lake sediments in the region which provides a useful basis for comparison, along with a review of terrestrial soil composition (Taylor et al. 2010).

Research in North America and Europe has shown that pesticide use in urban areas often exceeds that in rural areas – possibly as a result of effective management of agricultural practices, while cumulative urban and domestic use of these products has increased without strong oversight (Paul & Meyer 2008, Wittmer 2009). This report provides the information obtained in a preliminary investigation of the presence of contaminants in the sediments of urban streams in Hamilton and their potential toxicity to aquatic biota. Inputs and effects of dissolved or waterborne contaminants have not been addressed in the present study.

1.2 Site selection, contaminant analysis and toxicity testing

In June 2011 twenty-five sites in urban streams in Hamilton were selected for sediment sampling. The investigation focussed on three catchments with varying degrees of urban and rural development, namely the Mangakotukutuku, within which the Peacockes, Rukuhia and Te Anau branches were sampled, the Kirikiriroa which drains northeastern Hamilton and the Waitawhiriwhiri catchment in west Hamilton. The Mangakotukutuku is of particular interest because urban development is scheduled to proceed around the Peacockes tributary within the next 5 to 10 years, thereby providing the opportunity to study changes in stream ecology as urbanization proceeds, while comparing it with the Rukuhia and Te Anau branches. Both Waitawhiriwhiri and Kirikiriroa are typical examples of older urban development in Hamilton, with some rural influence in the upper catchments. Both up- and downstream locations were investigated within each catchment. Some sites were selected because we did not expect significant contamination, while others were selected based on our knowledge of potential impacts such as significant stormwater or sewage inputs, the location of old landfill sites, or current restoration projects (e.g., Bankwood stream). In 2012 metal concentrations measured in sediments collected in 2011 were used to select 16 sites for a repeat collection and an additional site (Ranfurly B) was sampled to confirm results from the previous survey. Samples collected in May 2012 were analysed for grain size, organic carbon content, metals, organochlorines, polycyclic aromatic hydrocarbons, and also used in a 10 day amphipod toxicity test.

Complementary research on dissolved contaminant concentrations and contaminant accumulation in biota is also being conducted as part of a graduate research project (T. Valler M.Sc candidate, U. Waikato, 2012).

1.3 Comparison with sediment quality guidelines

The ANZECC water quality guidelines provide Interim Sediment Quality Guidelines (ISQG, ANZECC Volume 1, Table 3.5.1.) for 10 metals and metalloids and a range of organic contaminants. These guidelines are not pass/fail criteria but are to be used to evaluate the potential effect of contaminants on biota, and the application of the guidelines depends on the goal of the investigation. If the site in question is being considered for remediation, comparison of contaminant concentrations with sediment quality guidelines should proceed in a stepwise manner. For example if contaminant concentrations in the whole sediment sample (<500 μm) exceed the Interim Sediment Quality Guidelines-Low (ISQG-L), this “triggers” a more detailed investigation into the site-specific bioavailability and potential toxicity of the contaminants (e.g., analysis of the fine (<63 μm) sediment fraction, using a weak acid digestion to extract readily “bioavailable” metals). If the site in question is a high value site for conservation then ideally contaminant concentrations should be undetectable against background concentrations for the region. Comparison with ISQG can therefore help identify sites with minimal contamination that can be investigated further (e.g., comparison with local or regional reference sites) for protection for conservation purposes. Due to a lack of suitable high quality data (worldwide) the ISQG are derived from international databases and should be interpreted while taking local conditions into account.

Toxicity testing of sediments using species such as amphipods is one way to take into account both the presence of multiple contaminants and the influence of mitigating factors such as high concentrations of organic matter that will render some contaminants less

bioavailable and toxic to biota. High concentrations of organic matter can, however, generate high concentrations of ammonia and sulphides which can cause toxicity. Sediment sampling and processing for toxicity testing usually results in the loss of these porewater contaminants which is a test artefact that is difficult to mitigate (see Section 3.3). We did not sample sediment porewaters for these contaminants.

1.4 Establishing current “background” concentrations and contaminant sources

The present study was a preliminary survey of Hamilton streams and we did not explicitly select a site to represent “background” or “reference” conditions. Instead, as recommended by ANZECC (2000) we have compared element concentrations across local sites and identified outliers that may indicate contamination has occurred, or is occurring. We arbitrarily identified a range (i.e., $\geq 3x$ greater than median concentrations Tables B-1 and B-2) to classify a concentration as an outlier, and also took into account:

1. the range of variation in element concentrations across sites in the present study with the knowledge that some sites are likely to be impacted by urban or rural influences, and
2. the ISQG as described in section 1.3, and
3. background concentrations in terrestrial soils ($<500 \mu\text{m}$) in the Waikato region (Taylor et al. 2010).

As part of a long term study Taylor et al. (2010) defined sites in the Waikato region as “background” on the basis of their current land use and land use history, and used long-term forest sites “uninfluenced by anthropogenic activities for the life of the trees”. They provided a range of element concentrations in soils from these locations which, although terrestrial, enables us to distinguish element concentrations associated with background geology from anthropogenic contamination and other influences.

A goal of the present study is to establish current conditions in urban streams in Hamilton and to identify the presence of contaminants that may potentially inhibit the success of restoration efforts. Contaminant sources can sometimes be identified by a characteristic suite of elements and we expected that urban stormwater and rural fertilizer use would have an influence at some locations (Table 1-1). In Hamilton many waterways, and the Mangakotukutuku catchment in particular, drain peat swamp land and as a result orange iron (Fe) precipitates (or flocs) are often observed on the surface of stream sediments where iron-rich groundwater meets oxygenated surface waters causing the precipitation of Fe compounds. In addition Fe bacteria can metabolise the Fe in groundwater and form insoluble ferric compounds in orange-coloured bacterial mats. The presence of Fe flocs was noted during our field work as it may both physically and chemically affect stream fauna, because Fe compounds may sorb other elements such as phosphorus (P) and Zn.

Table 1-1: The suite of major elements or organic compounds typically associated with both current and historic sources in New Zealand. As, arsenic; B, boron; Ba, barium; Ca, calcium; Cd, cadmium; Co, cobalt; Cr, chromium; Cu, copper; F, fluorine; Fe, iron; Hg, mercury; K, potassium; Mg, magnesium; Mn, manganese; Mo, molybdenum; NH₄, ammonia; P, phosphorus; Pb, lead; Se, selenium; Sr, strontium; Zn, zinc.

Source	Elements	Organic contaminants
Urban stormwater	Cu, Zn and Pb	PAHs, TPH
Rural fertilizer use (excluding stock supplements listed below)	P, Cd, Ca and/or K and Mg (also B for brassica crops)	
Agricultural supplements for stock	Cu, Zn, Co, Mn, Se, Mo	
Horticultural pesticides and herbicides	As, Pb	OCs, OPs, glyphosate
Coal storage and coal ash	B, Ba, Sr	
Landfill leachate	Heavy metals and metalloids	NH ₄ , sulphides, organic carbon, wide range of organic compounds
Iron-rich groundwater from peat swamp	Fe (orange floc on stream sediments), Mn	
Horticultural fungicides	Cu	Various
Timber preservative	Cu, Cr, As	Various
Geothermal inputs	As, Hg, B, F	Sulphide

2 Methods

2.1 Site locations

In 2011, 25 sites were selected for sampling using GIS data for stream, road, and stormwater infrastructure locations and knowledge of historic and current land use in Hamilton (Table 2-1, Figure 2-1). In 2012 a subset of 16 sites were resampled, and a new site Ranfurly B was added to the study.

Table 2-1: Site information for 2011 and 2012 sampling. D/s, downstream; STW, stormwater; u/s, upstream. Grey highlighting indicates sites that were sampled again in 2012.

Stream	Label	Map Label	Site Information	Easting	Northing
Peacockes	A	PA	U/s of proposed STW detention. In June 2011 this was a small channel in a boggy paddock with overland flow. Probably ephemeral flow.	2713360	6371159
	B	PB	D/s of proposed STW detention for urban development. Large tributary, has riparian cover of moderately dense undergrowth and some trees at least 10m either side of stream	2713595	6373095
	C	PC	Mainstem Peacockes, integrates all u/s influences	2712800	6374003
	D	PD	Small tributary, has riparian cover of regenerating bush.	2713616	6373142
	E	PE	Major tributary, currently rural paddock, boggy.	2713328	6373225
	F	PF	Small tributary, mature pine? trees, no understorey, boggy, minimal flow.	2713850	6373621
Te Anau	A	TA	In Te Anau park, sewage impacted location (raw sewage periodically observed in stream in last couple of years), & 1.5 m diameter STW pipe u/s	2712240	6372979
	B	TB	Fitzroy park bridge, d/s of a couple of STW inputs. Recent improvements to sewage infrastructure u/s included large scale earthworks.	2712650	6373702
Rukuhia	A	RA	Sampled u/s of bridge over Saxby's road. Downstream of two small known STW inputs, rural landuse u/s.	2711098	6373041
	B	RB	D/s Ohaupo road, receiving inputs from road, and possibly nearby upholstery factory.	2711255	6373549
	C	RC	Tributary of mainstem receives 2 tributaries with entirely "old" urban inputs.	2712182	6374045
	D	RD	Mainstem of Rukuhia, good comparison for Peacockes C.	2712510	6374057
Normandy	A	NA	Location d/s of hospital, significant iron precipitates present, 900 mm diam STW pipe discharge u/s likely to drain new hospital carpark. Mature eucalypts in riparian zone, minimal understorey.	2711582	6374921
Waitawhiriwhiri	A	WA	Collected immediately u/s of outlet to Rotoroa lake (located adjacent to hockey club).	2710108	6375934
	B	WB	NOT COLLECTED South of Kahikatea Park, major drain from industrial area off Kahikatea Drive.	-	-

Stream	Label	Map Label	Site Information	Easting	Northing
	C	WC	NOT COLLECTED Rural landuse –only “drains” visible in aerial photographs.	-	
	D	WD	D/s of railway and State Highway 1 inputs.	2708456	6377744
	E	WE	Old landfill u/s Edgecumbe Park off Charlemont Street.	2709767	6378467
Bankwood	A	BA	Urban park, site of restoration studies (D. Rowe, NIWA).	2710276	6380357
Kirikiriroa	A	KA	Rural location, narrow drain through paddock, iron floc deposits, deep layer of sludge.	2712397	6381001
	B	KB	Impacted site located in grassed urban park with minimal vegetation on banks. Old landfill upstream, stream has very high conductivity. Large vents for landfill located approximately 5 m from sampling site.	2710196	6381969
	C	KC	Mainstem location, sampled above likely river influence.	2709495	6381723
	D	KD	Located in grassed urban park, u/s of Thomas Road. Likely to be influenced by new urban development.	2711119	6383267
	E	KE	Likely to be influenced by old urban inputs, located off Glen Lynne Road.	2710374	6381608
Ranfury	A	RN_A	Located in grassed urban park, with minimal vegetation on banks. Was in flood at time of 2011 sample collection.	2710715	6378805
	B	RN_B	Upstream of RN_A, in privately owned gully off Bettina Ave. <i>Only sampled in 2012.</i>		
Parana	A	PR_A	Located in urban park garden, fish monitoring site (B. Bartels, NIWA).	2711711	6376926
Graham	A	GA	Located in grassed urban (archery) park off Cobham Drive, minimal vegetation on banks.	2711432	6375312

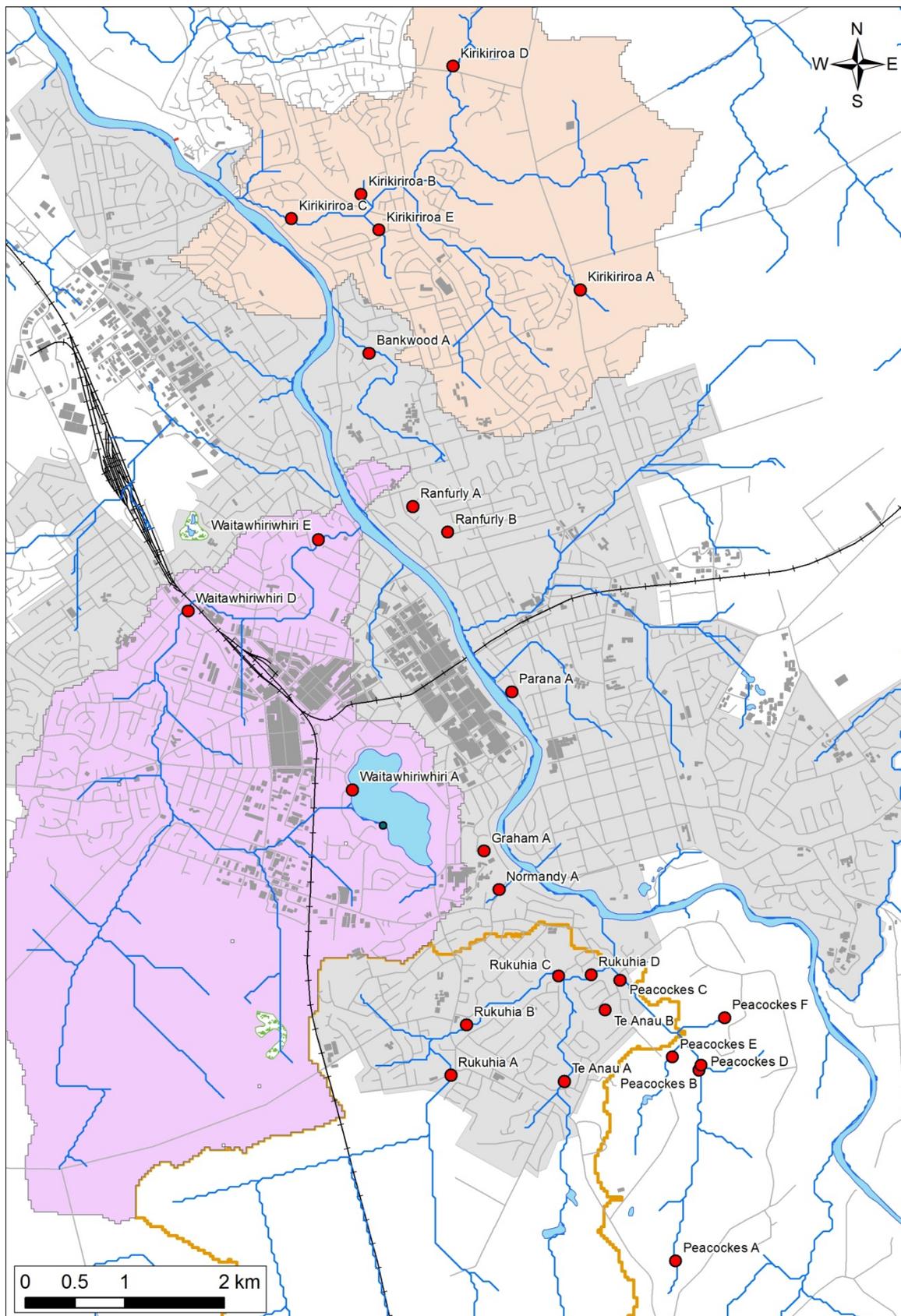


Figure 2-1: Map of Hamilton indicating the sampling locations for sediments.

2.2 Sediment collection

Sediment samples were collected (downstream to upstream) from multiple settling zones in the streams where fine sediment had accumulated, using a plastic trowel and removing the top 20 mm (approximately) of sediment (see Section 2.3.5 for discussion of fine sediments and metal bioavailability to biota). Approximately 1.5 to 3 kg of sediment was collected from each site. Sediment (and some water) was collected in two clean plastic ziplock bags, mixed thoroughly within and between bags to ensure the samples were homogenous, double-bagged and placed on ice for transport back to the laboratory. Waterway characteristics were noted using the Waikato Regional Council Qualitative Habitat Assessment Field Datasheets for wadeable streams and sampling locations were noted using GPS. In 2011 high flows were occurring in many of the waterways when we sampled which prevented us from observing whether iron flocs were present on the benthos. In 2012 the presence or absence of iron floc was noted at all 17 sites sampled. At the laboratory samples were either used immediately for contaminant analysis or frozen. One sample from each location was used for measurement of contaminants. In 2012 one sample was used for amphipod toxicity testing (never frozen). Any remaining sediment was frozen for future analyses (-20°C).

2.3 Sediment analysis

2.3.1 Dry matter

Sediments were dried for 4 to 22 hours at 103°C to remove free water prior to analysis, and then weighed to determine moisture content (Detection Limit (DL) 0.40 g 100 g⁻¹ as received) (Hill Laboratories, Hamilton, New Zealand).

2.3.2 Particle size analysis

In 2011 sediments were wet-sieved to separate the fractions greater than and less than 500 µm, and then the different size classes were weighed (DL = 0.4 g 100 g⁻¹ dry weight) (Hill Laboratories, Hamilton, New Zealand). In 2012 samples were analysed by Malvern Laser Sizer particle size analysis (Earth Sciences Department, Waikato University, Hamilton).

2.3.3 Total organic carbon

Samples were subjected to acid pre-treatment to remove carbonates if present. Organic carbon content was then measured by Elementar Combustion Analyser (DL 0.05g 100 g⁻¹ dry weight) (Hill Laboratories, Hamilton, New Zealand).

2.3.4 Total recoverable metals <500 µm fraction

A subset of the sediment samples was wet-sieved to obtain the <500 µm fraction, and digested to extract total recoverable metals using hot concentrated nitric and hydrochloric acid (US EPA protocol 200.2). Copper, Pb and Zn concentrations were measured in the <500 µm fraction using ICP-MS (Hill Laboratories, Hamilton, New Zealand) (Detection Limit (DL) 2, 0.4 and 4 mg kg⁻¹ respectively). Subsequently these sediment digests were also analysed using ICP-MS for a wider suite of up to 27 metals and metalloids by the University of Waikato, as part of a collaborative graduate research project.

2.3.5 Fine sediment (<63 µm) fraction

A subset of the sediment samples obtained in 2012 were wet-sieved to obtain the <63 µm fraction, and digested in 2 M HCl at room temperature, in an end-over-end shaker for 24 hours to extract “bioavailable” metals (solid:liquid 1:50 w/v) (Williamson & Wilcock 1994) (Hill Laboratories, Hamilton, New Zealand). Copper, lead and zinc concentrations were measured in the <63 µm fraction using ICP-MS (Hill Laboratories, Hamilton, New Zealand) (DL, 1, 0.2 and 2 mg kg⁻¹ respectively). Subsequently these sediment digests were also analysed using ICP-MS for a suite of 22 metals and metalloids by the University of Waikato.

“Bioavailable” metals are operationally defined by the analytical procedure summarized above, which was developed for extraction of metals from marine sediments (ARC 1994). This procedure was developed to attempt to characterize the fraction of metals present in sediments that are more labile and likely to interact with aquatic organisms (for various reasons), than metals that are extracted from the <500 µm fraction by US EPA protocol 200.2 using hot, acidic digestion. The fine sediments present in the <63 µm fraction are more likely to be ingested by aquatic organisms (either deliberately or incidentally) and then be subjected to acidic or alkaline digestion at ambient temperatures in the gastrointestinal tract. In addition fine sediments have a large surface area to volume ratio and can bind a high proportion of metals present in sediments. Metals readily extracted by “weak” acid digestion from fine sediments are also those more likely to be labile and dissolved in sediment porewaters and overlying water, thereby interacting with sediment-dwelling organisms via gill- and other epidermal surfaces as dissolved metals.

It is also useful to measure contaminants in the fine sediment fraction because these particles, with their high surface area to size ratio, often not only bind a large portion of the contaminants in sediments, but are also the particles most readily transported through waterways. Fine sediments accumulate (by definition) in depositional areas and can contribute dissolved contaminants to porewaters. The fine sediment fraction will be the most ‘ecologically relevant’ for contaminant bioavailability in sandy to gravelly sediments. At muddy locations, it is likely to be more useful to examine the contaminant load in the <500 µm fraction.

2.3.6 Organochlorine analysis

Dried sediments were sonicated, and subjected to Solid Phase Extraction (SPE) clean-up to extract organochlorines (OCs) (Hill Laboratories, Hamilton, New Zealand). Samples were then analysed on dual column Gas Chromatograph-Electron Capture Detector to measure organochlorines (modified US EPA protocol 8082).

2.3.7 Polycyclic aromatic hydrocarbons

Samples (as received) were sonicated, diluted and subjected to SPE clean-up (if required) to extract polycyclic aromatic hydrocarbons (PAHs). Samples were then analysed using Gas Chromatograph-Mass Spectrometry Selected Ion Monitoring analysis (modified US EPA protocol 8270).

2.4 Amphipod toxicity testing

Sediments collected on the 7/5/2012 and 8/5/2012, were stored at 1°C until 10 and 11/5/2012, when they were sieved to remove the >500 µm fraction. Small amounts of Dechlorinated Hamilton City Tapwater (DHCT) were added as necessary to complete the sieving, and no water was discarded to avoid loss of contaminants. Sufficient slurry of the <500 µm fraction was added to three 680 mL plastic containers to create a 25 to 30 mm layer of sediment and the solutions were left to settle in a constant temperature room at 12°C. The containers were loosely covered with cling film and a plastic lid to minimise evaporation. Five days later gentle aeration was commenced in each container. Eight days (18/5/12) after the sediments were added to the containers, the majority of fine particles had settled out, so the overlying water was removed by siphoning, and remaining sediment layer was mixed and adjusted to sediment layers of 20 to 25 mm. A circular layer of plastic film was placed on the sediment surface to prevent mixing of the sediment and water, and approximately 580 mL of DHCT was gently added. The plastic film was removed and gentle aeration recommenced. A 20 mm x 100 mm piece of mesh was added to each container, and positioned to extend out of the sediment and provide firm substrate for the amphipods if required as we were not interested in mortality due to amphipods being smothered by fine sediments.

On two occasions (14/5/12, and 28/5/12) amphipods were collected from the littoral zone of Lake Rotorua, near the outlet of Hamurana Stream (2796212E, 6346832N). Approximately the top 20 mm of sediment was collected and transported to Hamilton with a shallow layer of overlying water. On 14/5/12 the sediments were sieved to separate both >2 mm fraction and the <500 µm fraction prior to transport; on 28/5/12 only the >2 mm fraction was removed. At the laboratory DHCT was added to the overlying water and the sediments were held in a constant temperature room (12 to 17°C), with constant aeration. On 14/5/12, <500 µm sediments from Lake Rotorua (primarily fine sand, with small amounts of silt) were added to six 680 mL plastic containers (for control treatment replicates) in a layer approximately 25 mm deep and approximately 580 mL of DHCT was gently added onto a layer of plastic covering the sediment. The plastic film was removed and the sediments were left to equilibrate until 18/5/12 when overlying water was removed in all containers as described above. Air temperature was increased to 15°C on 18/5/12.

Air temperature was increased to 17°C on 21/5/12 because we expected to start the toxicity test that day, however insufficient numbers of amphipods were available from the first collection of sediments (held in the laboratory in the 500 µm to 2 mm fraction with approximately 30% by volume of < 500 µm sediments). After the second collection of amphipods on 28/5/12 the constant temperature room setting was decreased to 15°C to more closely match the surface water temperature at Lake Rotorua of 13°C.

On 29/5/12 amphipods were sieved from Lake Rotorua sediments and amphipods were hand-picked from the >500 µm fraction and counted into groups of 10. Twenty amphipods were added to each of the sediment replicates. Thereafter the test was monitored daily to check aeration, to count and remove amphipod mortalities, and to monitor water quality (pH, dissolved oxygen, temperature and conductivity; see Appendix C). After ten days (8/6/12) the amphipods were sieved from the sediments and counted to determine survival rates.

3 Results and Discussion

3.1 Grain size and organic carbon content

Sediments were collected from settling zones at each location, and will not be representative of the substrate particle size composition of the entire stream channel. This was estimated while samples were being collected and at the majority of sites was primarily sandy with some fines. Sediments at Waitawhiriwhiri A had a slightly higher gravel content, and at Kirikiriroa A sediments were entirely fine mud. Particles greater than 2 mm were removed from the samples prior to laser analysis. Samples from Peacockes B, E and F had >40% silt and clay content as did Waitawhiriwhiri A and Ranfurly A (Figure 3-1). Kirikiriroa A had no visible hard substrate in the stream channel. Rukuhia D, Normandy A, Bankwood A, Kirikiriroa B and Parana A sediment samples had >40% coarse sand content.

The average organic carbon content of the <500 μm fraction was 4%, and ranged from 1.4% at Rukuhia D to 9.8% at Peacockes B (Figure 3-2).

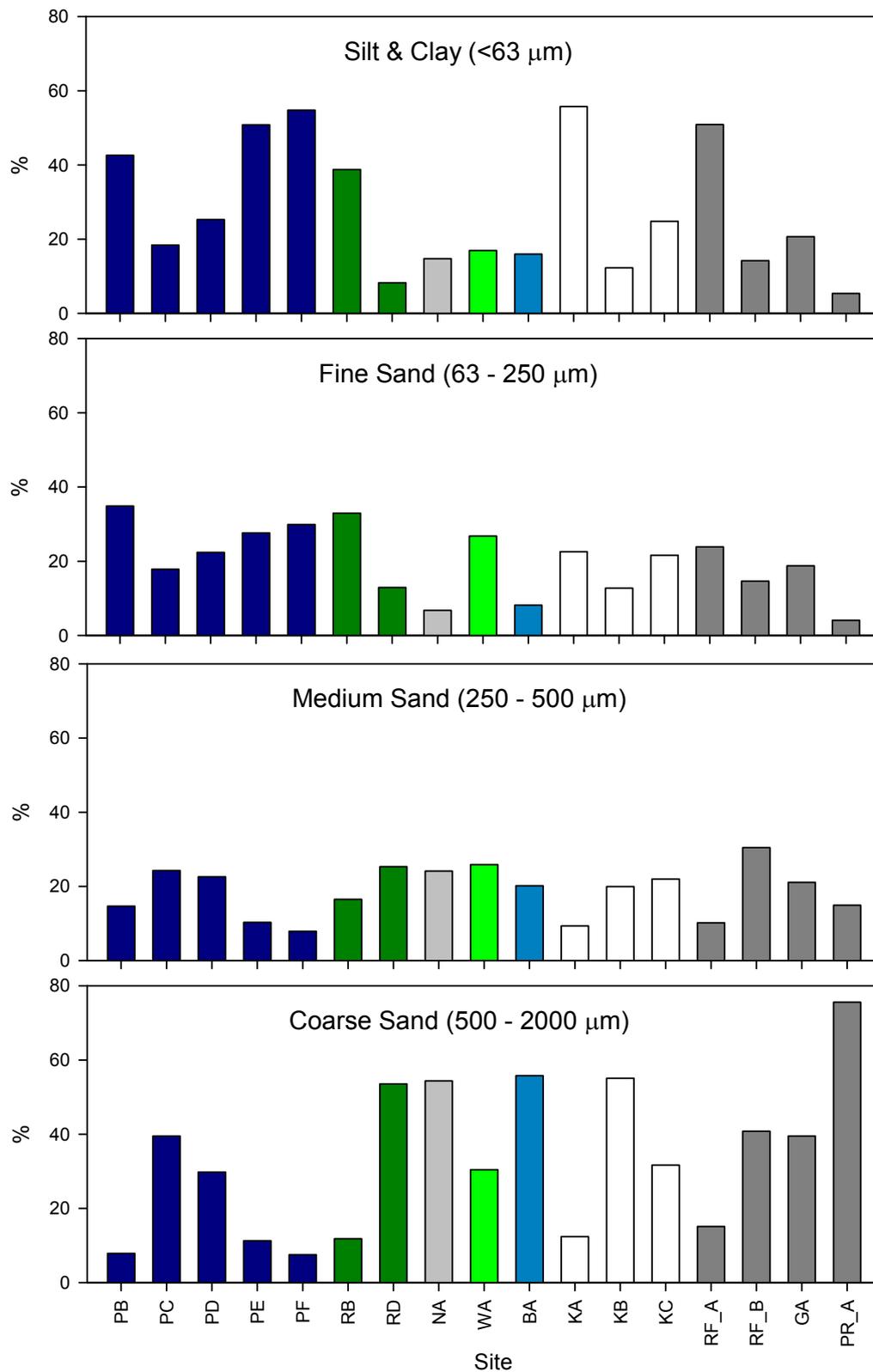


Figure 3-1: Size class distribution of particles <2 mm in urban sediments collected in 2012.

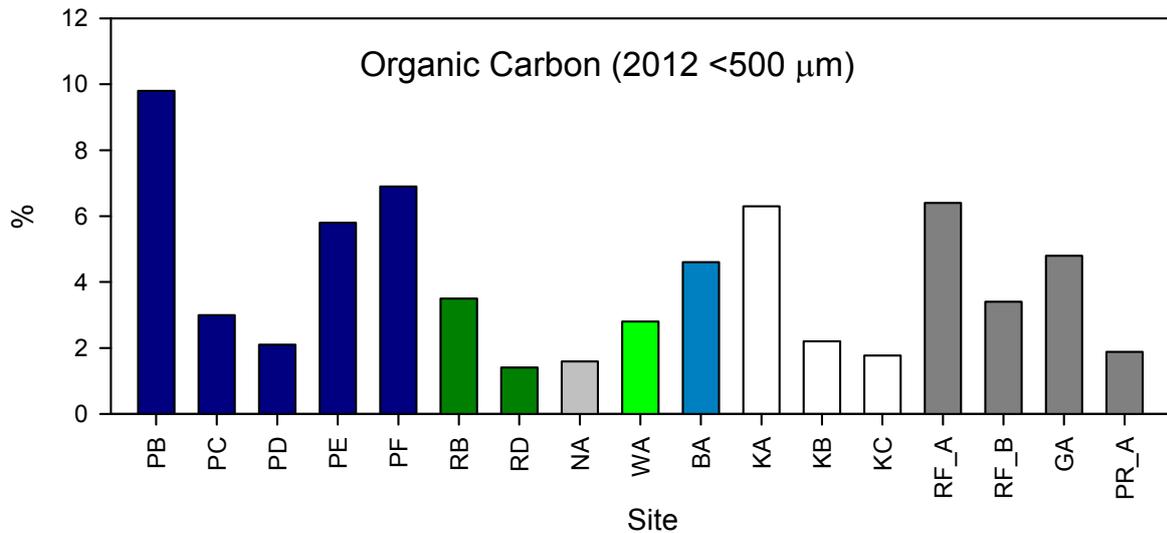


Figure 3-2: Percentage organic carbon measured in the <500 μm sediment fraction in 2012. Key to site labels in Table 2-1.

3.2 Sediment organochlorines and polycyclic aromatic hydrocarbons

Of the 25 organochlorines and 16 PAH's measured by Hill Laboratories only 10 of the PAH's were greater than the detection limit of the assay. The PAH's were only detected at 7 out of 17 of the sites sampled in 2012 (Table 3-1, Figures A-7 and A-8). The ISQG for PAHs are for concentrations normalised to 1% organic carbon. At the sites where PAHs were detected, organic carbon concentrations ranged from 1.9% at Graham A to 6.4% at Ranfurly A. None of the ISQG-Low trigger values available for 6 out of the 10 compounds were exceeded by PAH concentrations normalised to 1% OC including the values for summed low or high molecular weight PAHs (as defined by ANZECC 2000) (Figure 3-3).

Table 3-1: Polycyclic aromatic hydrocarbon concentrations and organic carbon (OC) content (%) measured in urban sediments in 2012. Interim Sediment Quality Guidelines Low (ISQG-L) refers to the ANZECC (2000) sediment quality guidelines for each contaminant. See footer for PAH abbreviations.

Site	OC %	B[a]A	B[a]P	B[b]F	B[g,h,i]P	B[k]F	Chry	FA	IPyr	Phe	Pyr
(μg kg ⁻¹ dry wt normalised to 1%OC)											
WA	2.8	136	182	218	150	89	125	186	89	71	225
BA	4.6	9
KB	2.2	14
RF_A	6.4	22	25	38	31	19	22	33	20	.	28
RF_B	3.4	18	26	35	29	15	21	35	18	15	44
PA	4.8	13	13	19	13	8	13	25	.	13	29
GA	1.9	27	32	37	32	21	27	43	21	27	53
ISQG-Low	-	261	430	-	-	-	384	600	-	240	665

B[a]A, benzo[a]anthracene; B[a]P, benzo[a]pyrene; B[b]F, benzo[b]fluoranthene + benzo[j]fluoranthene; B[g,h,i]P, benzo[g,h,i]perylene; B[k]F, benzo[k]fluoranthene; Chry, chrysene; FA, fluoranthene; IPyr, indeno(1,2,3-c,d)pyrene; Phe, phenanthrene; Pyr, pyrene.

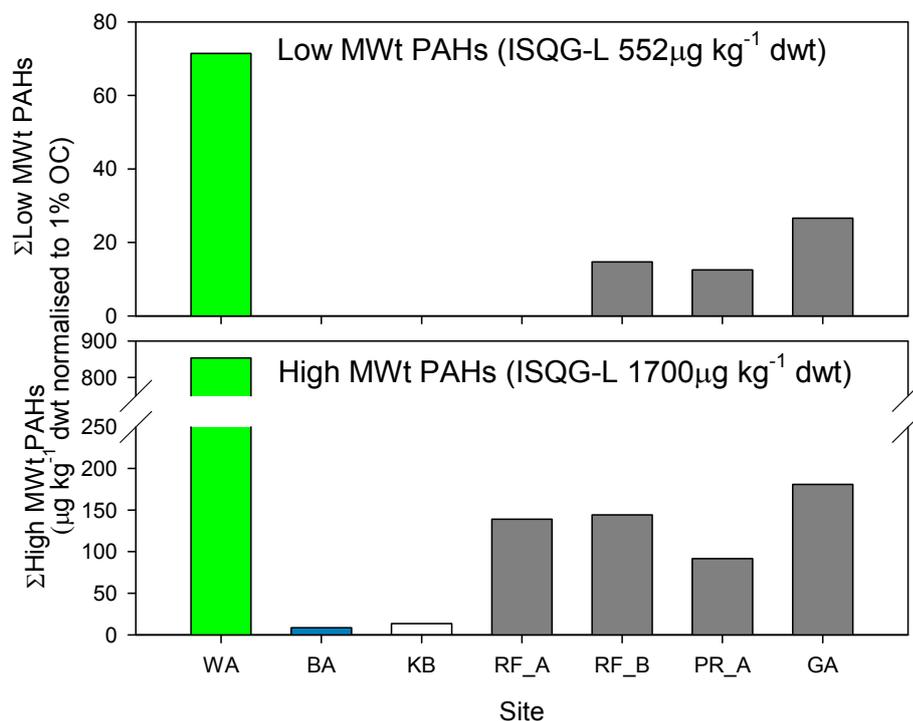


Figure 3-3: Concentrations of low molecular weight (MWt) or high MWt PAHs in Hamilton's urban sediments collected in 2012. The ISQG-Low for low MWt PAHs is $552 \mu\text{g } 1\% \text{OC}^{-1}$, and for high MWt PAHs is $1700 \mu\text{g } 1\% \text{OC}^{-1}$.

3.3 Amphipod toxicity test

The 18 d equilibration period between sieving the sediments and addition of the amphipods allows sediment chemistry to return to conditions similar to those at the sampling sites. Some contaminants may however have been released from the sediments, or their bioavailability and toxicity may have been altered. Artefacts of laboratory-based sediment toxicity testing are difficult to avoid.

Dissolved oxygen was $10.2 \pm 0.3 \text{ mg L}^{-1}$, and water temperatures were $15.5 \pm 0.5^\circ\text{C}$ in all treatments. Conductivity was $221 \pm 31 \mu\text{S cm}^{-1}$ in all treatments except Kirikiriroa B ($412 \pm 21 \mu\text{S cm}^{-1}$) and Normandy A ($451 \pm 34 \mu\text{S cm}^{-1}$). The pH was 7.5 ± 0.4 in all treatments except Kirikiriroa A (pH 6.1 ± 0.5), and Normandy A (8.4 ± 0.1). Multiple burrows were observed in at least one replicate of all sediments. No unusual behaviour was observed except for day 1 in the Waitawhiriwhiri A treatment. In two of the three Waitawhiriwhiri A replicates 12 to 14 of the amphipods were observed alive but above the sediment surface or on the water surface.

The average survival of amphipods exposed to sediments from Lake Rotorua (control; fine sandy sediment from source of amphipod collection) for 10 days was $93.3 \pm 1.5\%$ (Figure 3-4). Survival was greater than or equal to 90% in the majority of the urban sediments, apart from four locations, Normandy A ($85\% \pm 2$), Peacockes D ($88.3 \pm 1.2\%$), Kirikiriroa A ($76.7 \pm 2.5\%$) and Waitawhiriwhiri A ($66.7 \pm 5.5\%$). Survival was significantly lower in Waitawhiriwhiri A sediments than in the control sediments, and those from Rukuhia B ($95 \pm 0\%$), Kirikiriroa C ($95 \pm 1.7\%$), Ranfurly A ($97 \pm 0.6\%$) and Graham A ($95 \pm 0\%$) ($F = 2.03$, $P < 0.03$).

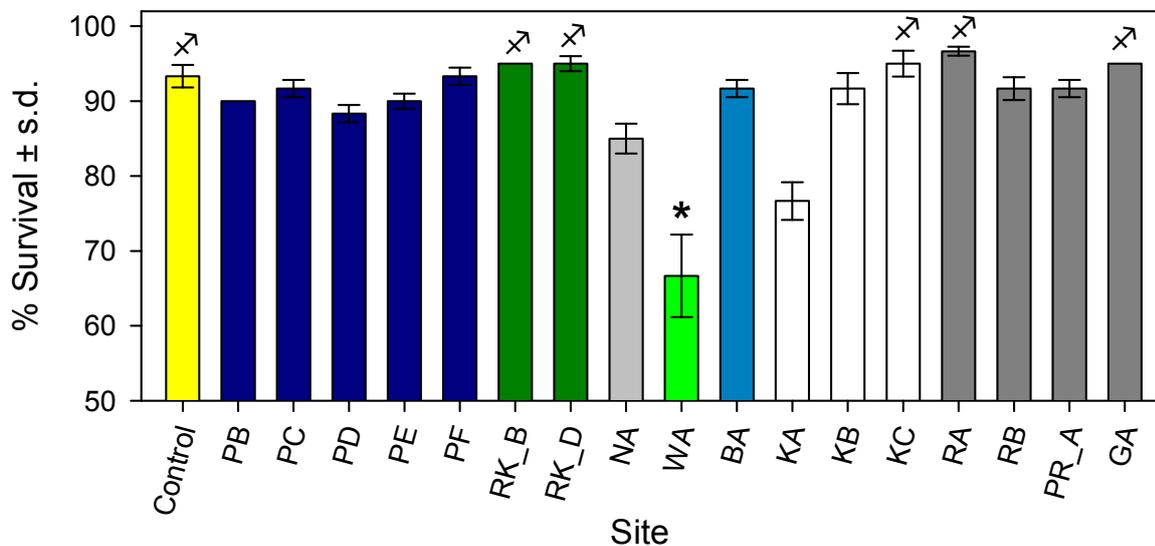


Figure 3-4: Percentage survival of amphipods after exposure to urban sediments for 10 days. Asterisk indicates survival significantly lower than in sediments with the anchor symbol.

3.4 Sediment metals 2011 and 2012

In 2011 and 2012 the Cu, Zn and Pb concentrations measured by the University of Waikato correlated well with those measured by Hill Laboratories ($R^2 < 500 \mu\text{m}$ 2011 Cu, Zn, Pb; 0.98, 0.99, 0.99), ($R^2 < 500 \mu\text{m}$ 2012 Cu, Zn, Pb 0.89, 0.89, 0.89), ($R^2 < 63 \mu\text{m}$ 2012 Cu, Zn, Pb 0.99, 0.996, 0.998) except for measurements of Cu, Zn and Pb at Ranfurly A in the $<500 \mu\text{m}$ fraction (Appendix A, Figures A1 to A6). Metal or metalloid concentrations measured by the University of Waikato in the $<500 \mu\text{m}$ fraction in both 2011 and 2012 and in the $<63 \mu\text{m}$ fraction in 2012 is provided below (Figures 3-5 to 3-10, Table 3-2, Figures A-7 to A-18 Appendix B), and concentrations for Cu, Zn and Pb are reported by Hill Laboratories are provided in Appendix A. The digests for Rukuhia B and D $<500 \mu\text{m}$ sediments were accidentally discarded prior to analysis by University of Waikato.

Each site was evaluated using either ISQG-L, ISQG-High (ISQG-H), Effects Range-Low (ER-L), or Effects Range-Median (ER-M) guidelines provided in ANZECC (2000) for 10 metals and metalloids. If no guidelines were available for an element, the concentrations were compared across all sites to establish background concentrations and outliers, as is recommended by ANZECC (2000). We took into account that many of the sites in the present study were selected because we expected that they would be contaminated by anthropogenic activity (Table 2-1), and designated values as outliers if contaminants were $\geq 3x$ median concentrations for the sediment fraction and year collected (Table B-1 medians; Table B-2 contaminant ratios). We note that for the purpose of evaluation we applied the sediment quality guidelines to the $<63 \mu\text{m}$ sediment fractions (which constitute a variable fraction of the sediments, 5 to 56%, Figure 3-1), despite the fact that they are intended primarily for comparison to the whole ($<500 \mu\text{m}$) sediment fraction. Application of the ISQG to the contaminant concentrations in the $<63 \mu\text{m}$ sediment fraction provides a potentially useful indication of contaminant bioavailability and toxicity to biota. Guideline exceedance

and amphipod toxicity test results for each location are summarised in section 3.5 below. Contaminant data and amphipod toxicity test results are summarised in narrative form for each “catchment” in sections 3.6 to 3.12 below, and Table 3-3.

For comparison the median and range of terrestrial soil concentrations of each element from background sites identified for the Waikato region by Taylor et al. (2010) are provided on the Figure for each element (<500 µm fraction). The analytical methods for terrestrial soils are different to the standard methods for aquatic sediments, however the concentrations were comparable for most elements excluding P for which Taylor et al. (2010) reported Olsens P. Further details are provided in Taylor et al. (2010).

The presence or absence of iron flocs was noted while sediments were being collected. In 2011 flows in many of the waterways were high and the water was turbid so iron flocs were only noted at 4 out of 25 sites (Figure 3-5). In 2012 we were able to observe the sediments at all 17 sites and iron flocs were observed at 10 of them (Figure 3-6). The flocs were particularly prevalent at Peacockes F and Kirikiriroa A, while at other locations they were not a dominant feature of the benthos.

In 2011 stream flows were much higher than in 2012 at most locations, and as a result samples taken in 2011 at Rukuhia B, Rukuhia D, Ranfurly A, Waitawhiriwhiri E and Kirikiriroa C may have had a stronger “terrestrial” signal than in 2012 because we were unable to access the main channel. For example at Ranfurly A, the stream was flowing over a grassed area that was exposed in 2012. Although we sampled from settling zones, we may have included soil from the banks that are not inundated during baseline flows. We have noted where this occurred in sections 3.6 to 3.12 below. The consistency of the data between 2011 and 2012 suggests that this has not significantly affected the results.

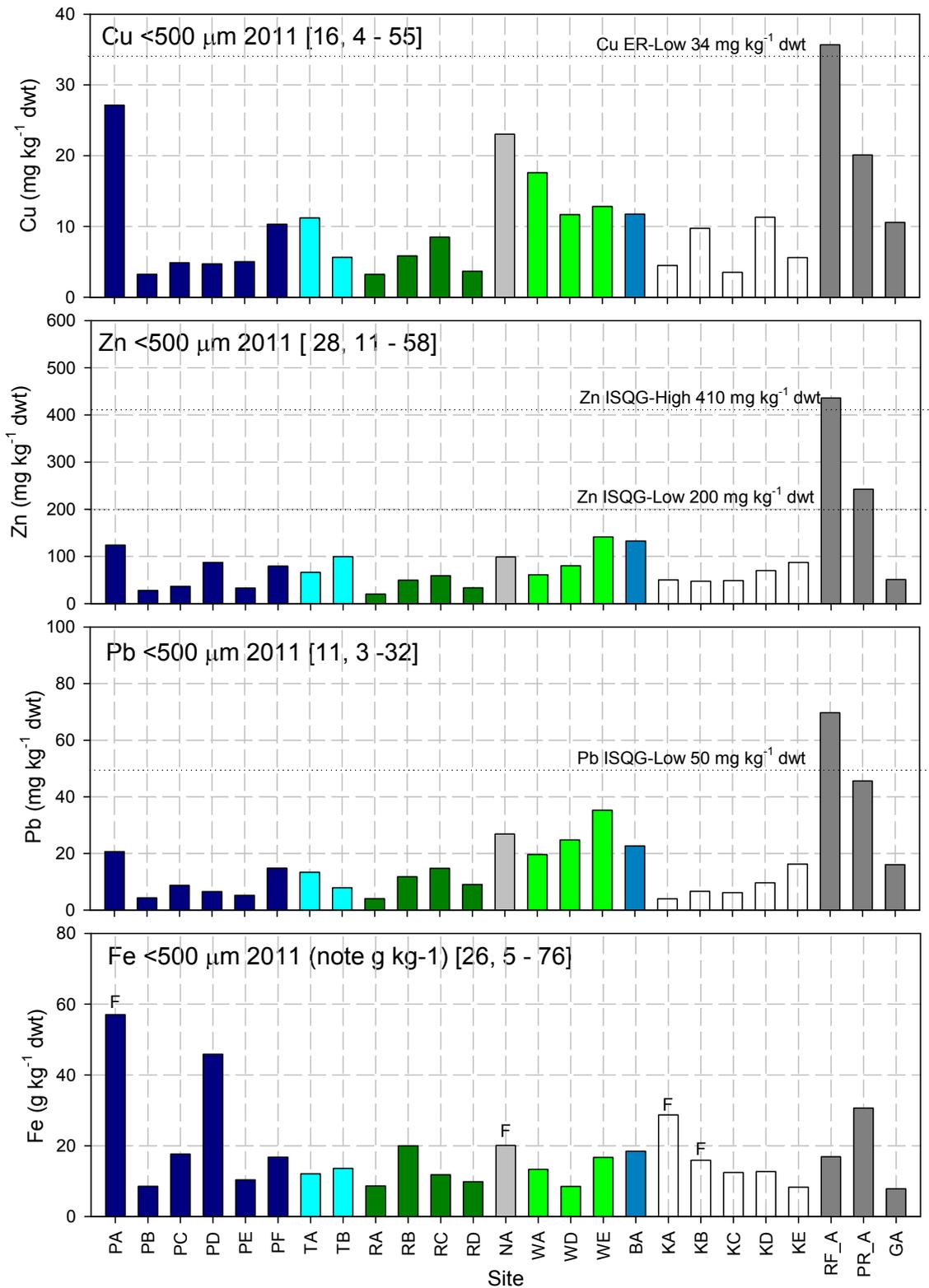


Figure 3-5: Copper (Cu), zinc (Zn), lead (Pb) and iron (Fe) concentrations measured in Hamilton's <500 μm urban sediments in 2011. Key to site labels is provided in Table 2-1. Terrestrial soil background concentrations are shown in square brackets (median, range). F = iron floc observed on sediment surface.

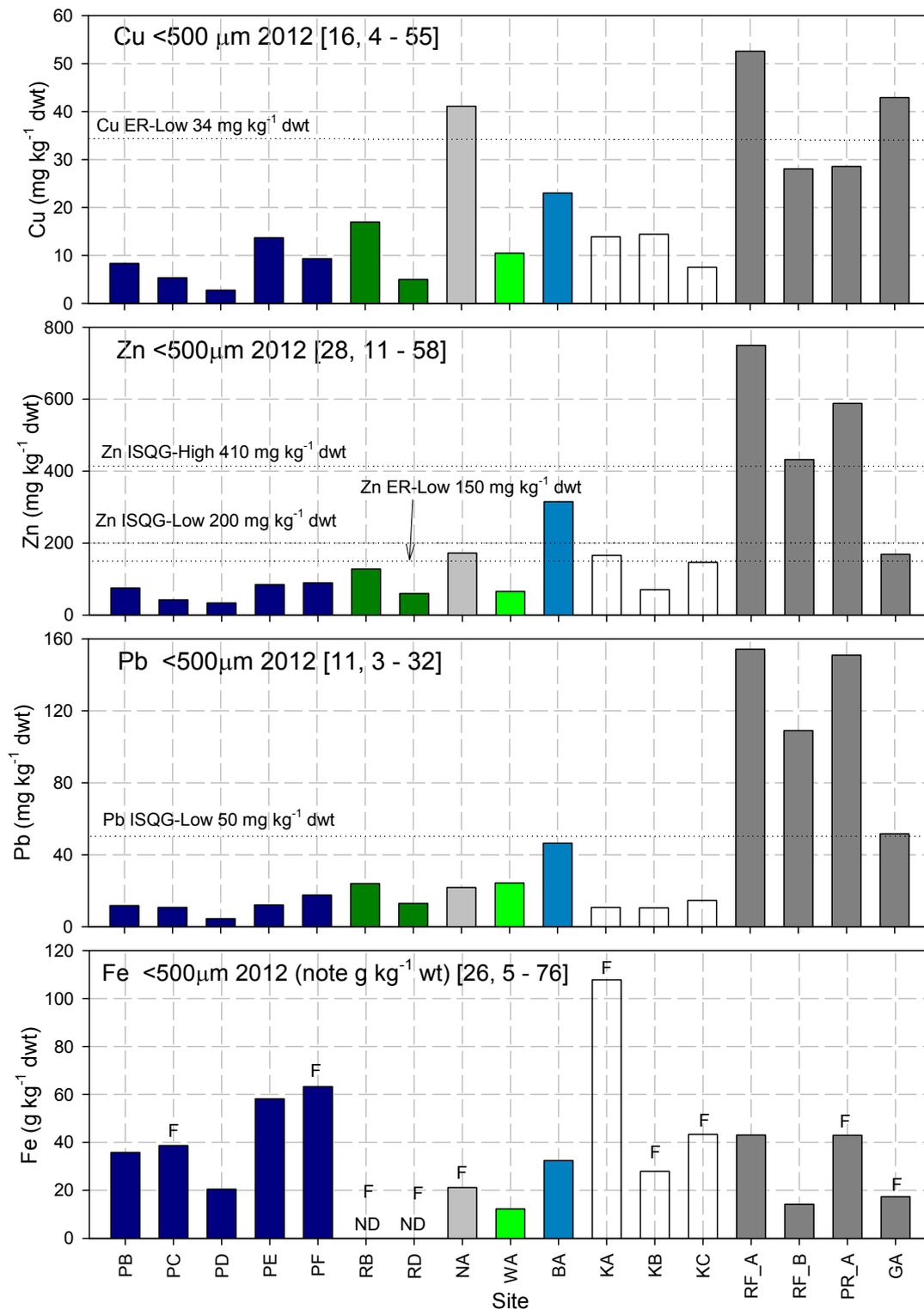


Figure 3-6: Copper (Cu), zinc (Zn), lead (Pb) and iron (Fe) concentrations measured in <500 μm sediments from Hamilton's urban streams in 2012. Key to site labels is provided in Table 2-1. Terrestrial soil background concentrations are shown in square brackets (median, range). F = Fe floc observed on sediment surface, ND = no data. Data for Rukuhia B and D was provided by Hill Laboratories.

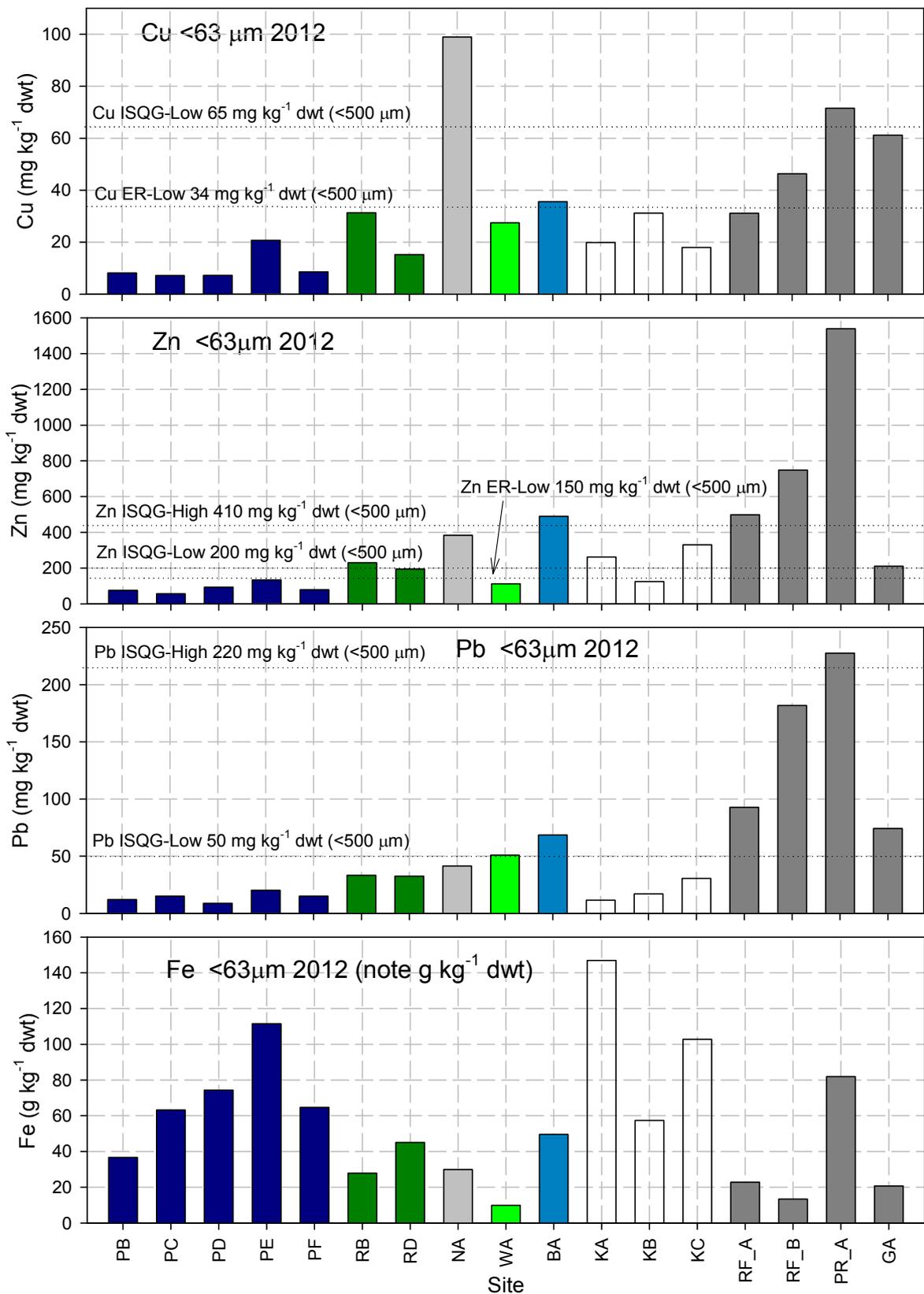


Figure 3-7: Copper (Cu), zinc (Zn), lead (Pb) and iron (Fe) concentrations measured in <63 μm sediments from Hamilton's urban streams in 2012. Key to site labels is provided in Table 2-1. Terrestrial soil background concentrations are shown in square brackets (median, range).

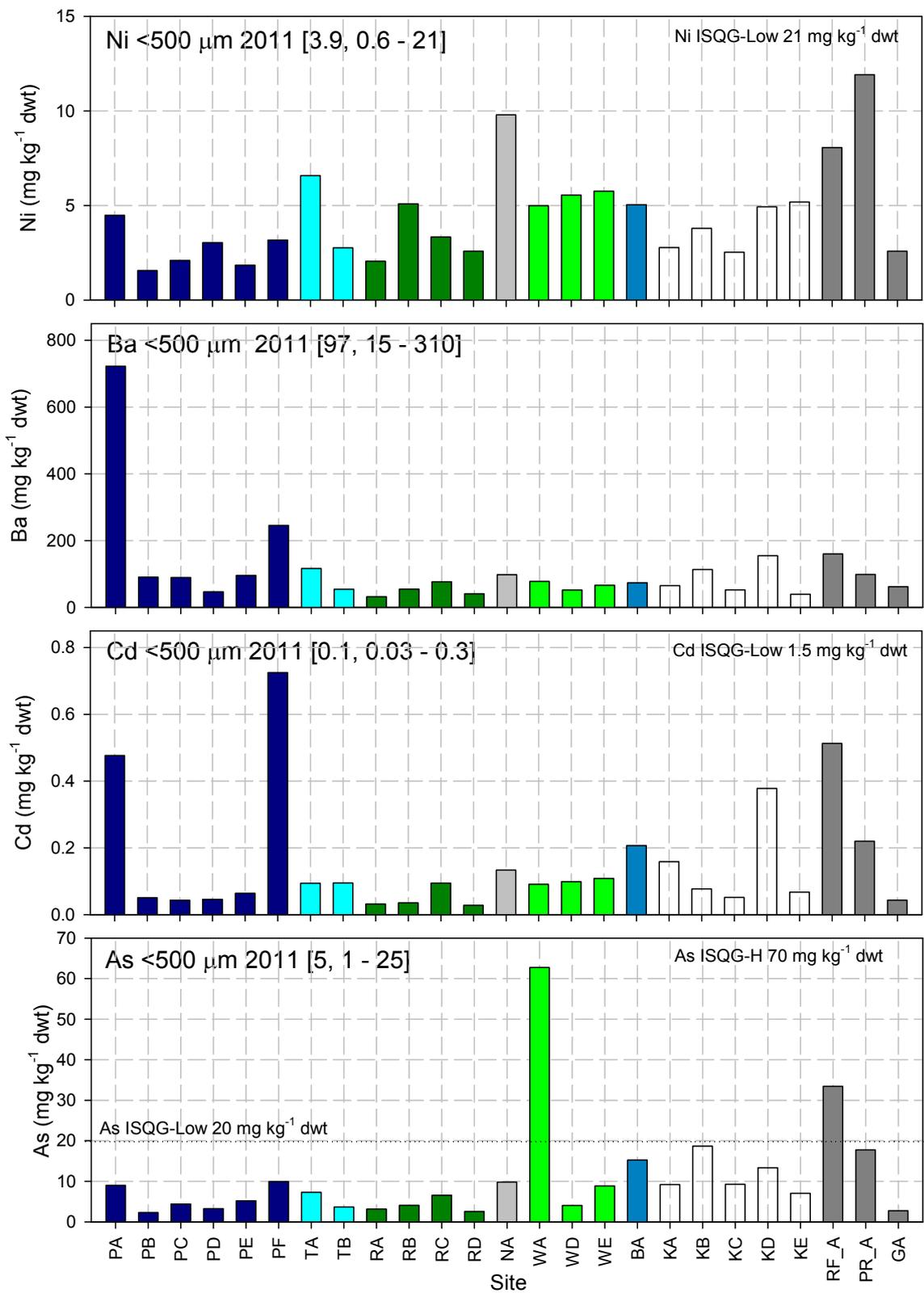


Figure 3-8: Nickel (Ni), barium (Ba), cadmium (Cd) and arsenic (As) concentrations measured in <500 μm sediments 2011. Key to site labels is provided in Table 2-1. Terrestrial soil background concentrations are shown in square brackets, (median, range).

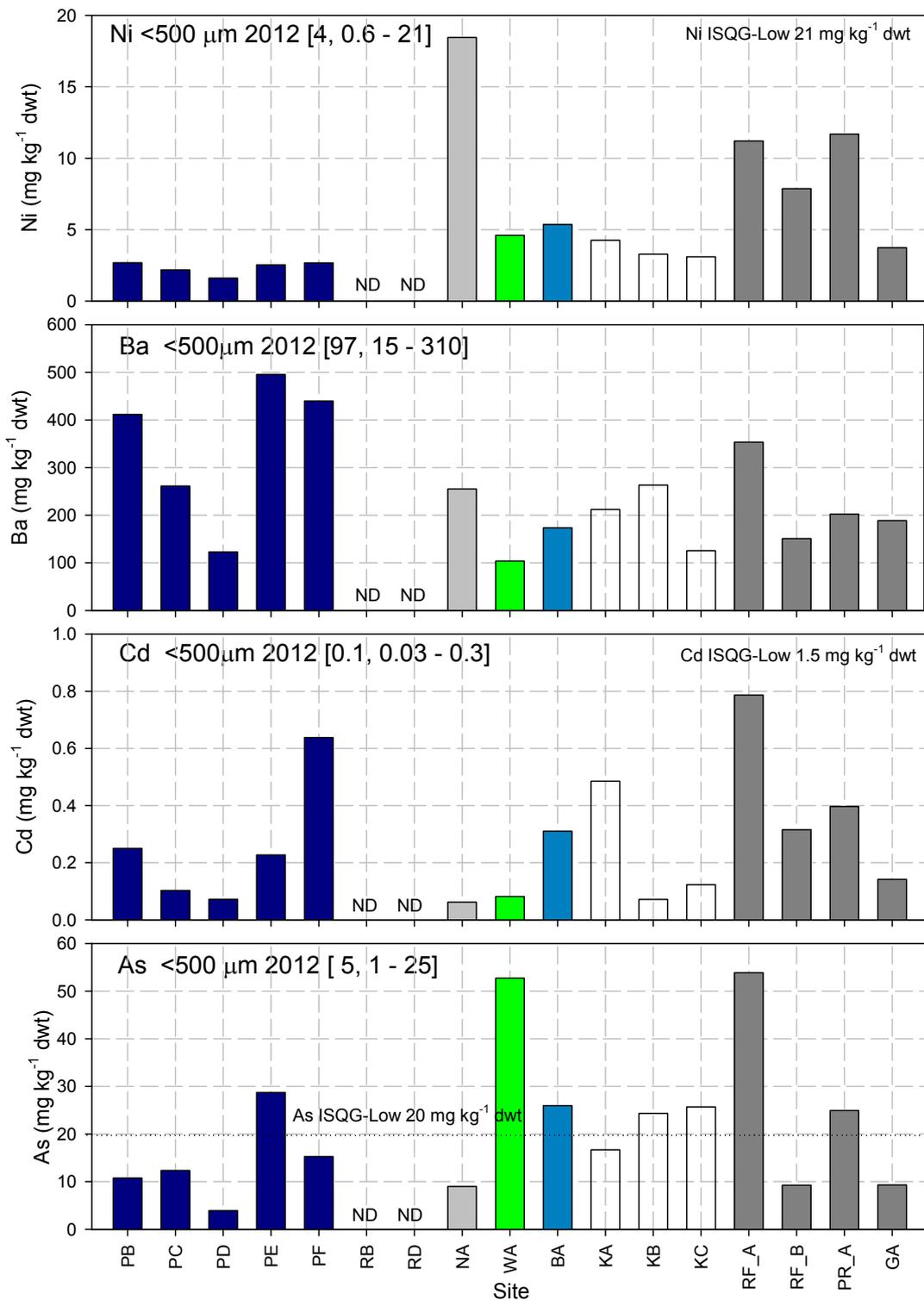


Figure 3-9: Nickel (Ni), barium (Ba), cadmium (Cd) and arsenic (As) concentrations measured in <500 μm sediments from Hamilton's urban streams in 2012. Key to site labels is provided in Table 2-1. Terrestrial soil background concentrations are shown in square brackets (median, range). ND = no data.

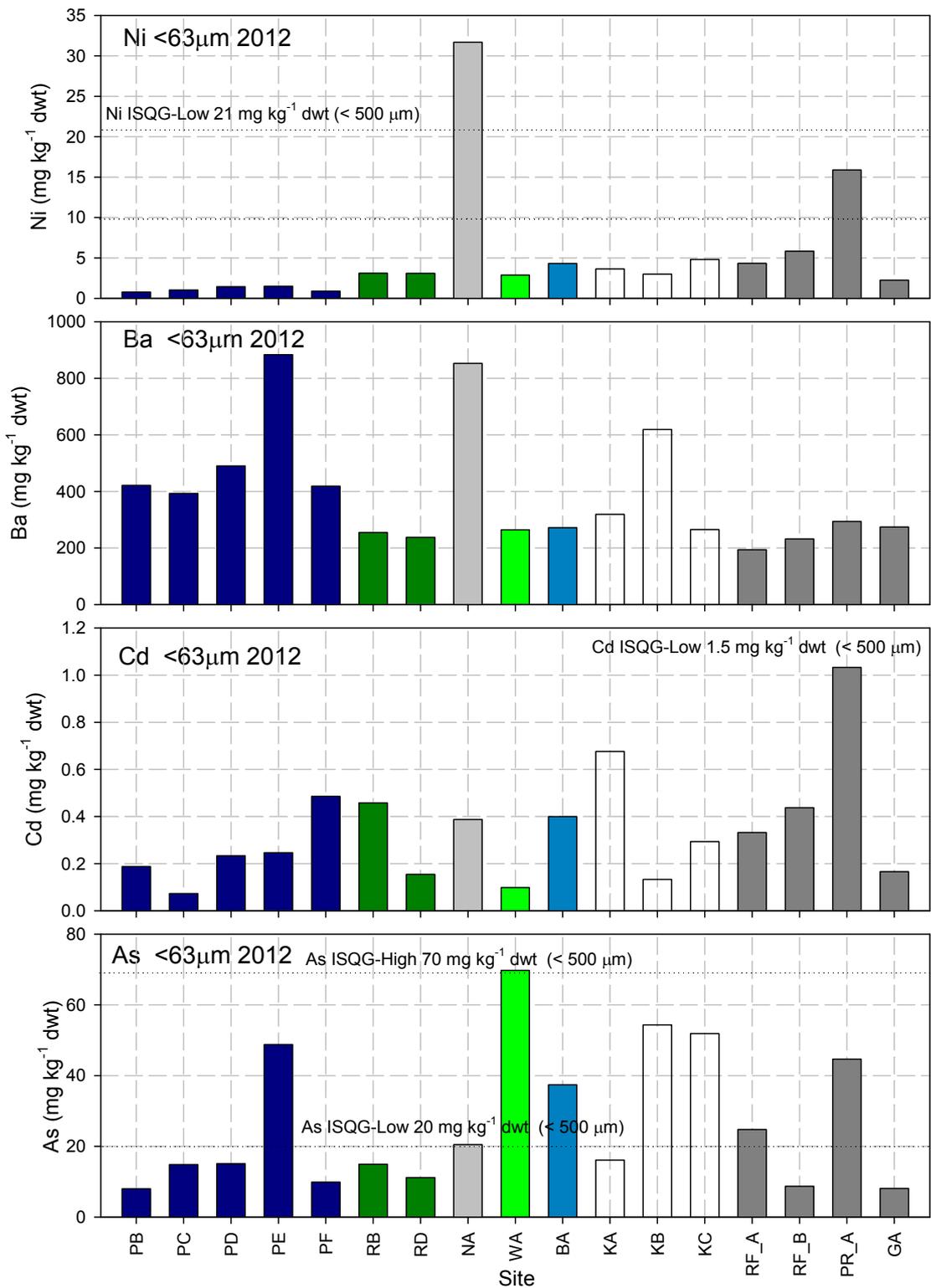


Figure 3-10: Nickel (Ni), barium (Ba), cadmium (Cd) and arsenic (As) concentrations measured in <63 μm sediments from Hamilton's urban streams in 2012. Key to site labels is provided in Table 2-1.

3.5 Summary of guideline exceedance and amphipod results for each site

In ANZECC (2000) sediment quality guidelines are used in a tiered investigation to determine whether it is likely that sediment-associated contaminants are likely to have effects on biota. Contaminant concentrations are compared with guideline values (ISQG-L and ISQG-H), and if guidelines are exceeded further investigation occurs. The information gathered is used in a weight-of-evidence approach to determine whether contaminants are likely to be affecting biota at the sampling location.

The ISQG-L are derived by correlation to a 10% probability of effects from a database on only a small number of species (that often includes several tests on amphipods because they are practical choice for sediment toxicity testing), while ISQG-H correlate to a 50% probability of effects (ANZECC 2000). The ISQG-L are a trigger value indicating that further investigation may be required, and effects on sediment biota are possible. The ISQG-High guidelines are represent contaminant concentrations at which effects are more likely (i.e., have been observed in 50% of the cases in the effects database)¹. Various options are available for more in depth investigation including:

- A. more detailed chemical characterisation of the sediments including factors that may influence contaminant bioavailability and toxicity, and
- B. toxicity testing (e.g., on amphipods and/or multiple species).

Amphipods are only one type of organism present in streams and a lack of toxicity in the present study does not mean all stream biota will be unaffected by contaminants present in the sediments. Ideally toxicity testing is conducted on a range of sensitive species from different phyla or classes (e.g., molluscs, insects, fish). There is very limited toxicity test data available to compare the contaminant sensitivity of native New Zealand species, but generally the amphipod *Paracalliope fluviatilis* is one of the most sensitive to Cd, Zn and Cu compared to species such as the mayfly *Deleatidium* sp. (Hickey 2000). The amphipod species used in the present study *Chaetocorophium lucasi* had only a slightly lower sensitivity to Cd than the mayfly, and was the species most sensitive to pentachlorophenol, and the second most sensitive to phenol (more sensitive than *Deleatidium* sp., sphaeriids or the freshwater shrimp *Paratya curvirostris*). Another consideration is that the bioavailability and toxicity of contaminants in sediments can be significantly altered by the process of sampling them and preparing them in the laboratory for toxicity testing (e.g., sieving to remove resident organisms). Contaminant bioavailability and toxicity can be increased or decreased by this process. A comparison of marine sediment toxicity testing *in situ* versus *in vitro* suggested that Cd toxicity to a marine population of the amphipod *C. lucasi* was equal to or slightly increased *in vitro* compared to *in vitro* exposures (DeWitt et al. 1999).

The ISQG and the amphipod toxicity test are therefore useful in a weight-of-evidence evaluation of likelihood of effects due to sediment-associated contaminants at the site of interest.

In the present study contaminant concentrations in sediments were compared to ISQG (ANZECC 2000) and summarized (Table 3-2). These guidelines were developed for

¹ ANZECC (2000) provides a detailed discussion of the derivation of sediment quality guidelines.

sediment size fractions <500 µm, however we also compared them to the <63 µm sediments to determine whether they correlated to the results of the 10 d amphipod toxicity test and whether this approach would be useful in future monitoring of urban sediments in Hamilton. For the same reason Cu and Zn concentrations were also compared to the more conservative sediment quality guidelines used by the US National Oceanic and Atmospheric Administration, and designated ER-L and ER-M (details in ANZECC 2000).

The ISQG-L were exceeded by the <500 µm sediments collected in 2012 at 8 locations in Hamilton, and ISQG-H were exceeded at 4 locations. Amphipod survival was statistically significantly decreased only in sediments from Waitawhiriwhiri A, where As exceeded ISQG-L in the <500 µm sediments (53 mg kg⁻¹ compared to 20 mg kg⁻¹ dwt), and met the ISQG-H for As (70 mg kg⁻¹) in the <63 µm sediment fraction (69.8 mg kg⁻¹). Also Pb concentrations exceeded the ISQG-L concentrations in the <63 µm sediments. Amphipod survival was below 90% at three other locations, Peacockes D, Normandy A and Kirikiriroa A, but there was no consistent relationship with guideline exceedances. No sediment quality guidelines were exceeded at Peacockes D and contaminant concentrations were generally low at this location. At Normandy A in 2012 only the <63 µm sediments exceeded ISQG-L for As, Cu, Ni and Zn. Similarly at Kirikiriroa A only the <63 µm sediments exceeded ISQG-L for Zn. Conversely Ranfurly A and B, Parana A, Graham A and Bankwood A are all notable because amphipod survival was 92% or higher but contaminant concentrations exceeded ISQG-L and ISQG-H for a range of contaminants in both sediment fractions. The more conservative ER-L guidelines for Cu and Zn also did not have a consistent relationship with the results of the 10 d amphipod test. The lack of toxicity despite guideline exceedance may be due to low bioavailability, for example as a result of the presence of dissolved organic matter or competing metal ions in the sediments.

In summary, application of the ISQG to the <500 µm sediments was predictive of the statistically significant effects observed in the Waitawhiriwhiri A sediments. The ISQG applied to the <63 µm sediment fraction was predictive of the more subtle effects on amphipod survival in Normandy A and Kirikiriroa A sediments but not those in the Peacockes D sediments. Considering the relative sensitivity of amphipods to other native freshwater fauna it is likely that these guidelines would be protective of most other native fauna. In future surveys of urban sediments in Hamilton we therefore recommend that the Cu, Zn, Pb, and As concentrations in the <63 µm sediment fraction, obtained by the Williamson & Wilcock (1994) method are compared to the ISQG in order to provide relative benchmarks of contaminant risks. It may also be useful to include Cd concentrations.

Table 3-2: Summary of sediment contamination and toxicity results for all sites, evaluated against sediment quality guidelines. Green = exceeds ER-L; Orange = exceeds ISQG-Low; Red = ISQG-High. Elements that exceed either ISQG-Low or ISQG-High guidelines are listed together and coloured red, but bold underlined elements are those that exceed ISQG-High. Grey shading indicates locations sampled in 2012.

Site	2011 ISQG <500um	2012 ISQG<500um	^A 2012 ISQG<63um	Amphipods %Survival	2011 ER-L <500um	2012 ER-L <500um	^A 2012 ER-L<63um	PAHs detected?
PA		-	-	-		-		
PB				90				
PC				92				
PD				88				
PE		As	As	90				
PF				93				
TA		-	-	-		-		
TB		-	-	-		-		
RK_A		-	-	-		-		
RK_B			Zn	95				
RK_C		-	-	-		-		
RK_D				95			Zn	
NA	Ag		As, Cu, Ni, Zn	85		Cu, Zn		
WA	As	As	<u>As</u> , Pb	67				Y
WD		-	-	-		-	-	
WE		-	-	-		-	-	
BA		As, Zn	<u>As</u> , Pb, <u>Zn</u>	92			Cu	Y
KA			Zn	77		Zn		
KB			As	92				Y
KC		As	As, Zn	95				
KD		-	-	-		-		
KE		-	-	-		-		
RF_A	As, Pb, <u>Zn</u>	As, Pb, <u>Zn</u>	As, Pb, <u>Zn</u>	97	Cu	Cu		Y
RF_B	-	Pb, <u>Zn</u>	Pb, <u>Zn</u>	92			Cu	Y
PR_A	Zn	As, Pb, <u>Zn</u>	As, Cu, <u>Pb</u> , <u>Zn</u>	92				Y
GA		Pb, <u>Ag</u>	Pb, Zn, <u>Ag</u>	95		Cu, Zn	Cu	Y

^AISQG have been applied to the <63 µm sediment fraction, however ISQG were derived from tests on the <500 µm fraction ANZECC (2000).

3.6 Peacockes tributary of the Mangakotukutuku stream

Peacockes A is located on an ephemeral waterway, characterised by overland flow through pasture. In 2011 we measured high concentrations of B, Ba, Cd, Co, Mn, P and Se in the sediments from this location, relative to other sites in the study and terrestrial background sites (Table 3-3).

All of these elements except Ba could have been enriched by fertilizer and stock supplement application (Cd is a contaminant of superphosphate). The elements, Co, Mn, and Se are used as stock supplements and B is used on brassica crops. Therefore in 2012, Peacockes A was excluded from the study in order to focus on permanently wetted areas of the waterway. Peacockes F had a similar contaminant profile to Peacockes A; in 2011 and 2012 relatively high concentrations of Ba, Cd, P, and Se were measured at Peacockes F which is surrounded by mature exotic trees and pasture. Like Peacockes A this small boggy tributary may dry out in summer months, and is probably affected by fertilizer application.

At the other 4 locations sampled on the Peacockes branch of the Mangakotukutuku, only As exceeded the ISQG-L at Peacockes E in 2012 – although As concentrations were not high relative to those at other locations in this study except in the 63 μm sediments. Peacockes E is located in a rural area and although it is probably a permanent waterway, at the time of sampling in 2012 included some overland flow over boggy pasture. Arsenic is a common contaminant in New Zealand, originating from geothermal discharges and anthropogenic uses including pesticides in sheep dips and horticulture, herbicides (e.g., for paspallum, particularly on school grounds), and as a timber preservative (copper-chromium-arsenic).

In the present study Ba concentrations ranged from 32 mg kg^{-1} dwt at Rukuhia A to 883 mg kg^{-1} at Peacockes E in the <63 μm fraction. In 2012 relatively high Ba concentrations were also measured in the <500 μm fraction at Peacockes E and F (496 and 440 mg kg^{-1} dwt respectively). Median background soil concentrations are 97 mg kg^{-1} dwt (range 15 – 310 mg kg^{-1} dwt) (Taylor et al. 2010). The element Ba is used in paint pigments, vacuum tubes, and in radiography, and is also found in high concentrations in some New Zealand coals. In the Peacockes catchment only contamination from paint or coal seems likely.

Peacockes B is on the mainstem of the tributary at the upper end of the catchment while Peacockes C is on the mainstem of this tributary just upstream of the confluence with the Rukuhia tributary. No ISQG were exceeded at either location and concentrations of all elements except Mn fell within the range measured at other urban locations in Hamilton, and background concentrations in terrestrial soils. Manganese is sometimes added to fertilizers or to stock supplements and the elevated concentrations measured at Peacockes, A, B, C, and E may reflect agricultural activity upstream in the catchment. There were no measurable concentrations of OC pesticides or PAH's in sediments from the Peacockes tributary.

Table 3-3: Summary of contaminant information for each site. Key to site labels is provided in Table 2-1. ND, no data; %S, percentage survival.

Site	2011 ISQG <500µm	2012 ISQG <500µm	^A 2012 ISQG <63 µm	Amphipods %Survival	Elements ≥ 3x median (see Table B-2)	Possible contaminant sources
PA		ND	ND	ND	Ag, B, Ba, Cd, Co, Cu, Fe, Mn, P, Se, Sr	Fertilizers, stock supplements
PB				90	Mn	Stock supplements/fertilizer
PC				92	Mn	Stock supplements/fertilizer
PD				88	Fe, V	
PE		As	As	90	As, B, Ba, Mn	Fertilizer, coal, paint, horticulture
PF				93	Al, Ba, Cd, Mn, P, Se	Fertilizers, stock supplements, coal
TA		ND	ND	ND	Al	Terrestrial sediment inputs?
TB		ND	ND	ND	-	-
RK_A		ND	ND	ND	-	-
RK_B			Zn	95	-	-
RK_C		ND	ND	ND	-	-
RK_D				95	-	-
NA	Ag		As, Cu, Ni, Zn	85	Ag, Al, Ba, B, Ca, Co, Cu, Mg, Na, Ni, Se, Sr	Historic landfill leachate, coal storage/coal ash disposal, chemical courier spill 2002, paints, pesticides, antifoulants
WA	As	As	As, Pb	67	As	Sodium arsenite weed spray (1950's), stormwater
WD		ND	ND	ND		
WE		ND	ND	ND	Pb	Historic road runoff
BA		As, Zn	As, Pb, Zn	92	Pb, Zn	Urban stormwater
KA			Zn	77	Fe, P, Tl	Fertilizer, iron floc
KB			As	92	As, B	Herbicides, landfill leachate
KC		As	As, Zn	95	As	Herbicides
KD		ND	ND	ND	Cd, Se	Fertilizer, stock supplements
KE		ND	ND	ND	-	-
RF_A	As, Pb, Zn	As, Pb, Zn	As, Pb, Zn	97	As, B, Ca, Cd, Cr, Cu, Mg, Ni, P, Pb, Se, Sr, Zn	Urban stormwater, historic horticulture/agriculture
RF_B	-	Pb, Zn	Pb, Zn	92	Pb, Zn	Urban stormwater
PR_A	Zn	As, Pb, Zn	As, Cu, Pb, Zn	92	As, B, Cd, Co, Cu, Na, Ni, Pb, Sr, Tl, Zn	Urban stormwater, historic horticulture/agriculture
GA		Pb, Ag	Pb, Zn, Ag	95	Ag, Cu, Pb	Urban stormwater

^AISQG have been applied to the <63 µm sediment fraction, however ISQG were derived from tests on the <500 µm fraction ANZECC (2000).

Amphipod survival ranged from 88% in sediments from Peacockes D to 93% in Peacockes F sediments. A relatively light layer of Fe floc was noted in most Peacockes sediments in the amphipod test, and burrows were noted in all replicates. There is no obvious reason why survival should be slightly lower in Peacockes D, and survival rates in all Peacockes sediments were not significantly different to those in the control treatment.

3.7 Rukuhia and Te Anau tributaries of the Mangakotukutuku stream

Both the Rukuhia and Te Anau tributaries are located in established urban areas of Hamilton. The sampling locations were downstream of known stormwater inputs and untreated sewage has been discharged upstream of Te Anau B in recent years (Mangakotukutuku Stream Care Group, Pollution Incident Register). Large earthworks have been completed in the vicinity of Te Anau B in recent stormwater upgrades. Rukuhia A was the most upstream location we sampled on this tributary. Council maps indicate two known small stormwater discharges just upstream and rural landuse above that. Rukuhia B is likely to receive input from Ohaupo Road while Rukuhia C, located further downstream, is in a large gully system surrounded by an established urban area. Rukuhia D can be compared directly to Peacockes C being located on the mainstem of the Rukuhia tributary just upstream of the confluence with the Peacockes tributary. Contaminant concentrations at the six Te Anau and Rukuhia sampling locations were all relatively low in 2011 and none exceeded ISQG-L or the ER-L. Only Rukuhia B and D were sampled in 2012 and again, contaminant concentrations were low, except for Zn in the <63 μm sediment fraction. The Zn concentrations of 230 and 195 mg kg^{-1} dwt at Rukuhia B and D in the <63 μm fraction respectively, exceeded or were just below the ISQG-L of 200 mg kg^{-1} dwt for Zn in <500 μm sediments. The ISQG-L for Zn were not exceeded by the <500 μm sediments from these locations in 2012 (128 and 60 mg kg^{-1} dwt, for RB and RD, measured by Hill Laboratories). There were no measurable concentrations of OC pesticides or PAH's in sediments from Rukuhia B or D. Amphipod survival was only tested in the Rukuhia B and D sediments in 2012 and was 95% in both sediments after 10 days exposure. Overall our data suggest that sediment contaminant concentrations in this branch of the Mangakotukutuku Stream are relatively low and generally not bioavailable or toxic to biota.

3.8 Normandy A and Graham A

These two streams are located close to one another however their different contaminant signatures suggest that Graham A is influenced primarily by urban stormwater, while Normandy A is likely to be influenced either by upstream inputs (e.g., groundwater leachate possibly from historic landfilling, bulk fuel storage and coal-fired boiler use in the area) and/or the legacy of a chemical spill on Normandy Road in 2002.

The Normandy Road spill occurred when a chemical courier truck caught fire and approximately 7000 L of chemicals were discharged onto the road, including formaldehyde, sodium hydroxide, spectrum biocide (alkyl dimethyl benzylammonium chloride in ethanol), pesticides (chlorfenvinphos), phosphoric acid, ethanol and methanol, aerosols, and paint (including marine antifouling paint) (N. Kim, 2012, presentation to WRC). As the fire was extinguished the chemicals were washed into the adjacent stormwater system discharging directly into Normandy Stream approximately 200 m upstream of its confluence with the Waikato River, and approximately 20 m downstream of where sediments were collected for

the present study. Although the stream pH decreased to 1, and Zn and Cu concentrations increased to 6000 and 3000 $\mu\text{g L}^{-1}$ respectively immediately after the incident, all 3 parameters were close to pre-spill conditions within 3 days. The strongly acidic conditions are thought to have assisted in flushing the chemicals through the waterway to the Waikato River where they were diluted.

A preliminary site report suggests that the historic land fill location in the upstream catchment is likely to be on the Lorne St side of the hospital near the boiler house, although, landfilling could have been more widespread (WRC DOC #1648376).

Normandy A had the most elevated concentrations of a wide range of contaminants compared to other locations in the present study. In 2011, Ag concentrations were 1.1 mg kg^{-1} dwt in the <500 μm sediments, exceeding the ISQG-L of 1.0 mg kg^{-1} dwt. In 2012 Ag was 0.2 mg kg^{-1} dwt in the <500 μm fraction and 0.7 mg kg^{-1} dwt in the <63 μm fraction. Boron, Ni, and Sr concentrations were also elevated compared to other Hamilton locations, and background Waikato soils in both 2011 and 2012, in the <500 μm and <63 μm sediments. In the <63 μm fraction Al, Ba, Ca, Co, Cu, Mg, Na, and Se also were elevated above concentrations at other Hamilton locations. Barium, B, Ni, and Sr are found in New Zealand coals. Boron in particular, is enriched in coal from the Waikato region. Waikato Hospital has used coal-fired boilers until the present day – the boilers were converted to gas powered systems in mid 2012. In the Waikato, median background soil concentrations of B are 3 mg kg^{-1} (Taylor et al. 2010) whereas they ranged from 16 to 213 mg kg^{-1} at Normandy A. Internationally terrestrial soils have background B concentrations of 3 to 300 mg kg^{-1} dwt and an average concentration of 30 mg kg^{-1} dwt, while sediments from the Great Lakes region in the 1990's had B concentrations of 0.5 to 7.9 mg kg^{-1} dwt (NLM 2012a). Of the other contaminants at the site, barium is commonly used as a white pigment in paints and may have been used in radiology since the 1940's, but compounds such as strontium were probably not used in radiotherapy until the 1970's. Cobalt is often discharged during industrial activities. Unpolluted freshwater sediments tend to have Co concentrations <20 mg kg^{-1} dwt (Kim & Gibb 2006), and concentrations <0.5 to 3 mg kg^{-1} dwt are considered deficient for raising cattle and sheep. Cobalt was 7 to 10 mg kg^{-1} dwt in the <500 μm fraction at Normandy and 22 mg kg^{-1} in the fine fraction; 6 mg kg^{-1} dwt is the median background soil concentration. Cobalt deficiency was a severe problem in New Zealand agriculture until the cause was identified in the 1930's, and rectified by addition of Co to fertilizer.

At Graham A, contaminant concentrations were relatively low in 2011, but in 2012 Pb, and Cu were slightly elevated in both sediment fractions while Ag concentrations were >8 mg kg^{-1} dwt and well above both guideline concentrations and concentrations at other locations. Given that Ag concentrations were within background soil concentrations in 2011 it is likely the 2012 result is an anomaly or "granule" effect rather than indicative of Ag contamination. Lead concentrations of 52 mg kg^{-1} dwt just exceeded the ISQG-L (50 mg kg^{-1} dwt), while Cu and Zn exceeded the ER-L in the <500 μm sediments. This contaminant suite is indicative of a low level of contamination by urban stormwater.

No OC's or PAHs were detectable at Normandy A, however, PAHs were measured in low concentrations at Graham A. Both individual PAH concentrations and the sum of low or high molecular weight guidelines were well below ISQG-L at Graham A.

Amphipod survival was 85% in Normandy A sediments and 95% in Graham A sediments, and not significantly different to survival in control sediments (93%). Only a light covering of Fe floc was observed on the surface of the sediments in the toxicity test; Fe floc was observed at both locations when sediments were collected. In the amphipod test the conductivity of the overlying water in the Normandy replicates was $451 \mu\text{S cm}^{-1}$ and pH was 8.4, compared to $221 \mu\text{S cm}^{-1}$ and pH 7.5 in most other treatments. Elevated contaminant concentrations at Normandy A may have caused the slight but not statistically significant decrease in amphipod survival.

3.9 Kirikiriroa catchment

The locations sampled in 2011 included Kirikiriroa A (a narrow, deep muddy waterway in a paddock) with only rural inputs upstream, Kirikiriroa B near an old closed landfill (in Tauhara Park near Wairere Drive), a “new” urban area (Kirikiriroa D –off Thomas Road in Rototuna), an “old” urban area² (Kirikiriroa E –in Tauhara Park, near Glen Lynne Road, Queenwood), and Kirikiriroa C on the mainstem of Kirikiriroa Stream.

In 2011 contaminant concentrations at all 5 locations were relatively low with the exception of KA where fertilizer application is likely to have increased sediment concentrations of P to $1659 \text{ mg kg}^{-1} \text{ dwt}$, and KD where Cd ($0.4 \text{ mg kg}^{-1} \text{ dwt}$) and Se ($0.9 \text{ mg kg}^{-1} \text{ dwt}$) concentrations were slightly elevated relative to other locations in Hamilton.

In 2012 only KA, KB and KC were sampled. The contaminant signature at KA suggests application of fertilizer because P was elevated 6 to 8x relative to median concentrations at other Hamilton locations. Iron concentrations were also high and abundant Fe floc was present on, and in, the water. Zinc concentrations of $262 \text{ mg kg}^{-1} \text{ dwt}$ in the $<63 \mu\text{m}$ sediments exceeded the ISQG-L for $<500 \mu\text{m}$ sediments ($200 \text{ mg kg}^{-1} \text{ dwt}$).

At both KB and KC, As concentrations in the $<500 \mu\text{m}$ sediments were 24 and $26 \text{ mg kg}^{-1} \text{ dwt}$ respectively and exceeded the ISQG-L of $20 \text{ mg kg}^{-1} \text{ dwt}$, but were similar to the upper range of concentrations found in background soils ($25 \text{ mg kg}^{-1} \text{ wt}$). Arsenic concentrations were 52 to 54 mg kg^{-1} at both sites in the $<63 \mu\text{m}$ sediments. Overall at both KB and KC, contaminant concentrations in the $<500 \mu\text{m}$ sediments were within the concentration range measured at other locations in this study and in background soils, but at KB in the $<63 \mu\text{m}$ fraction B was elevated relative to other sites. Boron is enriched in some New Zealand coals. Only one PAH, pyrene, was measurable in KB sediments at $14 \mu\text{g kg}^{-1} \text{ dwt}$ (normalised to 1% OC), which is well below the ISQG-L of $665 \mu\text{g kg}^{-1} \text{ dwt}$.

Amphipod survival was 77%, 92% and 95% in the KA, KB and KC sediments respectively, compared to 93% in the control sediments. Survival in the KA sediments was not statistically significantly different to that in the control sediments, however the data suggest an inhibition that could be the result of a 3 mm thick layer of Fe floc that formed on the sediments in all three replicates of this treatment during the toxicity test, or due to the low pH of the overlying water ($\text{pH } 6.1 \pm 0.5$). Large amounts of Fe floc were also observed at the collection site. Elevated Zn concentrations in the sediments may have also contributed to decreased survival rates, and the low pH (6.1) of the overlying water. The waterway at this location was a narrow trench through pasture with a deep layer of soft, muddy, anoxic sediments forming

² For Hamilton.

100% of the substrate. Large amounts of Fe floc were present along with an oily sheen on the water surface.

3.10 Waitawhiriwhiri catchment

Three locations were sampled in the Waitawhiriwhiri catchment. The outlet of Lake Rotoroa was designated Waitawhiriwhiri A, and sediments were sampled directly upstream of the outlet along the lake shore. The outlet discharges into an underground pipe which continues west under Innes Common. Waitawhiriwhiri D is on the mainstem of the waterway and was sampled off a layby on Avalon Drive. The sampling location is in a small gully downstream of several large stormwater pipes and culverts entering it from under Avalon Drive.

Waitawhiriwhiri E was sampled in Edgecumbe Park and is the mainstem of the waterway upstream of the confluence with the Waikato River. The decommissioned Willoughby Street landfill is located upstream of Waitawhiriwhiri E in Beetham Park to the southwest of Ulster Street.

In 1957 sodium arsenite was applied to Lake Rotoroa to control unwanted aquatic plants (Tanner & Clayton 1990). In 2011 As concentrations were 63 mg kg⁻¹ dwt in the <500 µm sediments and in 2012 we measured 53 mg kg⁻¹ dwt in the same sediment fraction. This is relatively high compared to concentrations of 5 to 25 mg kg⁻¹ dwt measured at most other locations we sampled in Hamilton and above the upper range of background soil concentrations (25 mg kg⁻¹). The ISQG-L and ISQG-M for As are 20 and 70 mg kg⁻¹ dwt respectively. Arsenic and Pb concentrations were 70 and 51 mg kg⁻¹ dwt respectively in the <63 µm fraction sampled in 2012. Concentrations of all other metals and metalloids were in the range measured at other locations in this study in both 2011 and 2012.

In 2008 a comprehensive study of Lake Rotoroa found high concentrations of several elements (including As, Cu, Zn, mercury (Hg), and Pb) and PAHs in the lake sediments (Rumsby 2008). Contaminant contour maps indicated that the location we sampled was the one of the least contaminated zones of the lake. Contaminant concentrations in 2008 were similar to those measured in the present study.

No organochlorines were detected, however PAH concentrations were highest at Waitawhiriwhiri A compared to the 17 other Hamilton locations we sampled in 2012. ISQG are only available for 6 of the 10 PAHs measurable in this study, but concentrations were well below the ISQG-L once normalized to 1% organic carbon (Table 3-1). Interim Sediment Quality Guidelines are also provided for summed low and high molecular weight PAH as defined by ANZECC (2000)³. The summed low molecular weight PAH concentrations were 71 µg kg⁻¹ dwt compared to the ISQG-L of 552 µg kg⁻¹ dwt, while the summed high molecular weight PAHs were 854 compared to the ISQG-L of 1700 µg kg⁻¹ dwt (Figure 3-3). Rumsby (2008) found that PAH exceeded ISQG-L at several locations and ISQG-H at only one location.

At Waitawhiriwhiri D and E all element concentrations were in the range of background concentrations measured in this study in 2011, except Pb at Waitawhiriwhiri E which was 3x median concentrations in the present study.

³ "Low molecular weight PAHs are the sum of concentrations of acenaphthene, acenaphthalene, anthracene, fluorene, 2-methylnaphthalene, naphthalene and phenanthrene; high molecular weight PAHs are the sum of concentrations of benzo(a)anthracene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene and pyrene.

Amphipod survival was only tested in Waitawhiriwhiri A sediments, and after 10 days exposure survival had decreased to 67% which was significantly lower than in control sediments (93%). It is most likely that decreased survival is due to the elevated As concentrations in the sediment which exceed ISQG-L, however other contaminants such as PAHs may have had a cumulative effect on survival. Cyanobacterial blooms are common Lake Rotoroa and it is possible that cyanotoxins are also present in the sediments. No Fe flocs were observed on the sediments at either Waitawhiriwhiri A, D or E.

3.11 Bankwood Park and Parana Park

In both 2011 and 2012 metal and metalloid concentrations at Bankwood Park were generally within the range measured at other locations in this study and in background soils. Both As ($37 \text{ mg kg}^{-1} \text{ dwt}$) and Zn ($315 \text{ mg kg}^{-1} \text{ dwt}$) concentrations however, exceed the ISQG-L for $<500 \mu\text{m}$ sediments of $20 \text{ mg kg}^{-1} \text{ dwt}$ for As and $200 \text{ mg kg}^{-1} \text{ dwt}$ for Zn. The As, Pb and Zn concentrations in the $<63 \mu\text{m}$ fraction were 37, 69 and $490 \text{ mg kg}^{-1} \text{ dwt}$ respectively. In 2012 Pb concentrations in the $<500 \mu\text{m}$ sediments were 3x the median concentrations at other locations in the study. No OCs were detected in Bankwood sediments and of the PAHs only pyrene was measurable at $9 \text{ ug kg}^{-1} \text{ dwt}$. Amphipod survival was 92% after 10 days and not significantly different to the control treatment despite the presence of a light layer of Fe floc on the sediments during the test.

In 2011 both Zn ($242 \text{ mg kg}^{-1} \text{ dwt}$) and Pb (46 mg kg^{-1}) concentrations in Parana Park sediments were higher than those at all other locations in this study except Ranfurly A, and Zn exceeded the ISQG-L. Similarly in 2012 Zn concentrations in the $<500 \mu\text{m}$ sediments were 589 mg kg^{-1} and exceeded the ISQG-H (410 mg kg^{-1}) while Pb concentrations were 151 mg kg^{-1} and exceeded the ISQG-L (50 mg kg^{-1}). In either the $<500 \mu\text{m}$ or $<63 \mu\text{m}$ sediments, a wide range of contaminants including As, B, Cd, Co, Cu, Na, Ni, Pb, Sr, and Tl were $\geq 3x$ median concentrations in the present study. No OCs were detected in the Parana A sediments, but 9 PAHs were present in measurable concentrations, although well below ISQG-L concentrations.

Despite the presence of these contaminants amphipod survival in sediments from Parana A was 92% after 10 days and not significantly different to that in the control sediments. A small amount of Fe floc was observed in the sediment toxicity test, creating a light layer on the sediment surface. Small amounts of Fe floc were observed at the sampling location upstream of where sediments were taken. This contaminant profile suggests urban stormwater inputs and historic horticulture or agricultural influences.

3.12 Ranfurly

Ranfurly A is located in Ranfurly Park, downstream of Ranfurly B which is in a gully behind Bettina Avenue, Claudelands. In 2011 Ranfurly A was sampled during high flows which had flooded the central channel onto the grassed banks. Copper (36 mg kg^{-1}), Zn (436 mg kg^{-1}) and Pb (70 mg kg^{-1}) concentrations were the highest measured in stream sediments at all locations in the present study and exceeded ISQG-L for Pb and ISQG-H for Zn. Arsenic, B, Cd, Cr, P, Se and Sr concentrations were also in the upper range of concentrations measured in this study ($\geq 3x$ median).

In 2012 flows were lower at Ranfurly A and we were able to sample closer to the main channel. Slightly higher Cu (53 mg kg^{-1}), Zn (750 mg kg^{-1}) and Pb (154 mg kg^{-1})

concentrations were present in the <500 μm sediments than in 2011 and concentrations exceeded those measured at all other locations in this study. In addition the same suite of metals and metalloids as in 2011 plus Ca, Mg, and Ni were at the upper concentration range of those measured at other locations in this study. In background soils median Cu, Zn and Pb concentrations are 16, 28, and 11 mg kg^{-1} respectively. Only Pb (93 mg kg^{-1}) was enriched in the <63 μm sediments at Ranfurly A relative to other locations.

Ranfurly B was sampled in 2012 and Cu (28 mg kg^{-1}), Zn (432 mg kg^{-1}) and Pb (109 mg kg^{-1}) concentrations at this upstream location were similar to those at Ranfurly A in the <500 μm sediments. In the fine sediments (<63 μm) Cu (46 mg kg^{-1}), Zn (748 mg kg^{-1}), Pb (182 mg kg^{-1}), and Cr (9 mg kg^{-1}) concentrations were also enriched relative to all other locations except Normandy A, Grahams A and Parana A.

No OCs were detected in sediments from Ranfurly A or B but a wide range of PAHs were measured in relatively low concentrations – with none exceeding guideline concentrations. Despite the relatively high concentrations of metals measured at both locations amphipod survival was 97% in Ranfurly A sediments and 92% in Ranfurly B sediments.

The contaminant signature in Ranfurly suggests urban stormwater inputs and possibly some historic As source (e.g., ex-horticultural or agricultural land use).

4 Conclusions

Considering the relative contaminant sensitivity of the amphipod *C. lucasi* to other native species in New Zealand (section 3.5) the results of the amphipod test suggest that although the sediments at some locations in Hamilton's urban streams are contaminated with a range of metals and metalloids above background concentrations in the region, their bioavailability and toxicity to the majority of aquatic biota are relatively low. Contaminant chemistry is however, affected by the process of sampling for laboratory ecotoxicological analyses and may differ to that *in situ*. For example, some contaminants may have been lost when overlying water was removed from the equilibrated sediments. Waitaiwhiriwhiri A, where sediments were collected from the lake shore near the outlet is an exception to the generally low sediment toxicity in this study, probably primarily due to the legacy of the sodium arsenite application to Rotoroa Lake for aquatic plant control in the 1950's. Other contaminants were present in the Rotoroa sediments, including Pb and PAHs and previous studies have demonstrated that urban stormwater has significantly impacted the lake (Rumsby 2008).

In the present study median Zn concentrations were 67 to 147 mg kg⁻¹ dwt in the <500 µm sediment fraction, compared to 28 mg kg⁻¹ in background soil concentrations from the region (Taylor et al. 2010). Almost all of Hamilton's urban streams have headwaters in rural areas and Kim (2011) and Taylor et al. (2010), suggest that widespread agricultural use of Zn supplements for facial eczema remedies has resulted in significant accumulation in farmed soils (median 62 mg kg⁻¹ dwt). Zinc is also a significant contaminant in urban stormwater. Our data suggest that Zn accumulation may be occurring in many of Hamilton's urban streams.

Contaminant concentrations in the Rukuhia and Te Anau branches of the Mangakotukutuku Stream were low suggesting the combination of rural inputs to the upper Rukuhia and Te Anau with established urban inputs to the lower sections of these catchments has resulted in minimal detectable contamination of the sediments in this waterway.

Contaminant signatures in the Peacockes branch of the Mangakotukutuku suggest that fertilizer application, agricultural supplements, or historic land use has resulted in some accumulation of contaminants. Amphipod survival was 88% to 95% in Rukuhia and Peacockes sediments indicating sediment-associated contaminant bioavailability and toxicity is low.

The limited sampling we conducted on the Waitawhiriwhiri catchment suggested that apart from Rotoroa Lake (Waitawhiriwhiri A), and Pb at Waitawhiriwhiri E metal and metalloid concentrations were relatively low in this catchment. Sediments in this catchment were not analysed for OCs or PAHs except at Rotoroa Lake, and amphipods were only exposed to sediments from Rotoroa Lake, limiting the inferences that can be made about the effects of sediment contaminants in this catchment.

The combination of large amounts of Fe floc and high concentrations of Zn may have decreased survival of amphipods in the muddy sediments from Kirikiriroa A. Arsenic concentrations exceeded ISQG-L lower in the catchment, and was 3x median concentrations at two locations but amphipod survival rates were high in these sediments. Our data suggest that sediment-associated contaminant bioavailability and toxicity is generally low in this catchment.

Of the other locations investigated in this study contaminant concentrations in Bankwood stream sediments were relatively low with the exception of Zn and Pb which were 3x median concentrations. Zinc and As exceeded ISQG-L but amphipod survival rates were high suggesting that sediment-associated contaminant bioavailability and toxicity is low in this waterway.

A wide range of contaminants were present at $\geq 3x$ median concentrations in the present study at Normandy A, Graham A, Parana A and the two sites Ranfurly A and B, suggesting that either historic or current contamination sources affect these waterways. Amphipod survival was greater than 90% at all of these locations except Normandy A. It is likely then, with the exception of Normandy A, that contaminant bioavailability and toxicity associated with the sediments at these locations is relatively low.

The most contaminated sites in the present study could have been identified by Zn, Pb, or As concentrations in the sediments that exceeded the ISQG-L guidelines in the $<63 \mu\text{m}$ fraction. Evaluating contaminant concentrations in just the $<500 \mu\text{m}$ sediments would not have identified Normandy A or Kirikiriroa A as impacted locations. In future surveys of urban contaminants in Hamilton we therefore recommend that sediments are analysed for Zn, Pb, Cu, and As in the $<63 \mu\text{m}$ fraction. Many urban locations in Hamilton are potentially influenced by agricultural activity upstream, therefore more thorough investigations could include Cd in the initial suite of contaminants as this may reveal legacy contamination or significant agricultural inputs.

The focus of the present study was on sediment-associated contaminants. Dissolved or waterborne contaminant concentrations can fluctuate significantly in urban streams, for example as a result of intermittent high volume stormwater discharges. The results of the present study cannot exclude the possibility that dissolved contaminants are significantly affecting stream biota in Hamilton's urban streams.

Some sites in Hamilton may be impacted by historical landfill leachate and we recommend therefore that future research includes sediment porewater sampling for ammonia and sulphide concentrations and porewater conductivity in addition to a suite of the contaminants measured in the present study. Finally, altered sedimentation rates in streams are common symptoms of urbanization that may have significant impacts on biota. Evaluation of sedimentation rates could prove useful to understanding loss of biodiversity in urban streams in Hamilton.

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Appendix A Sediment contaminant concentrations

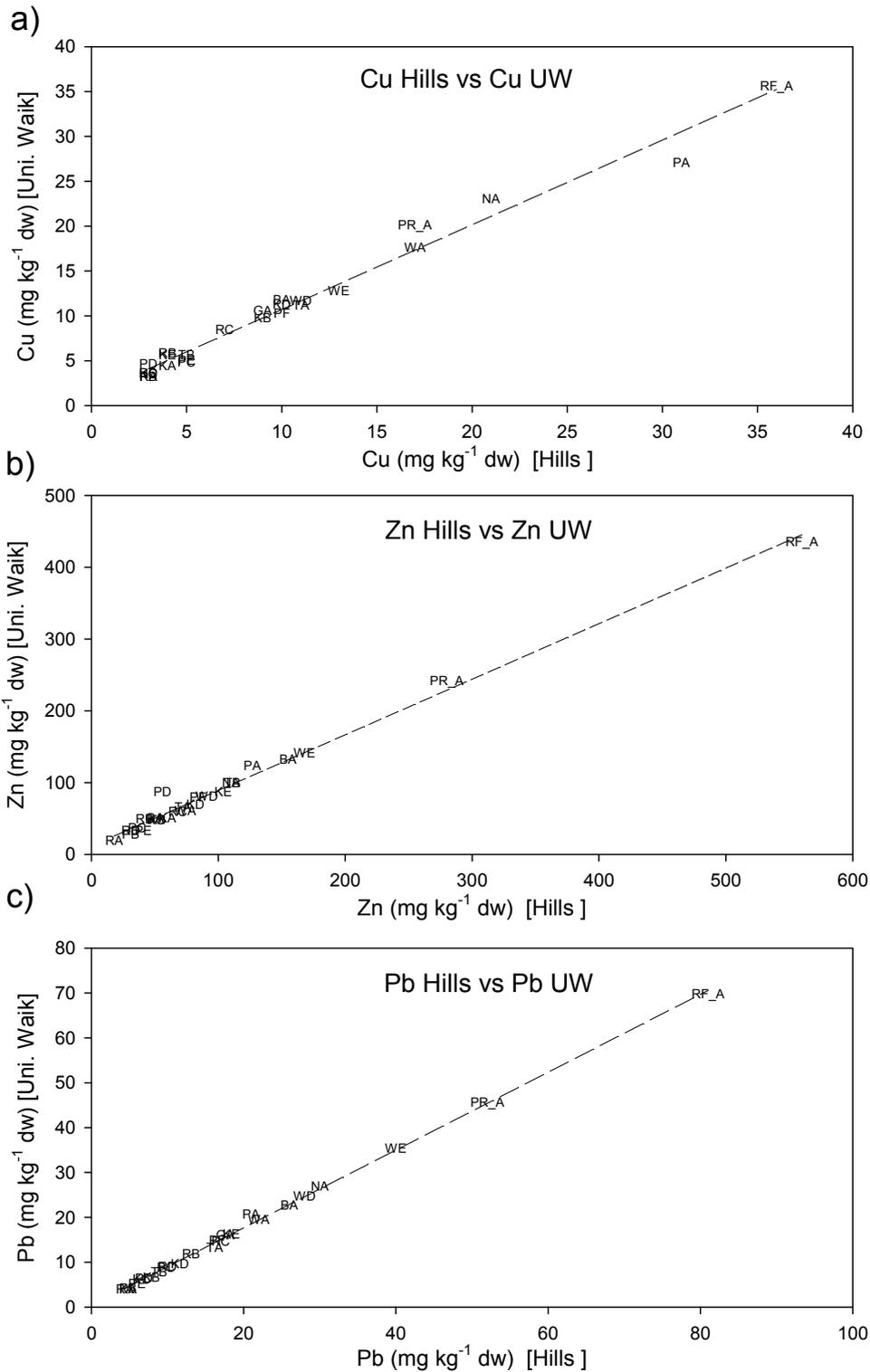


Figure A-1: Comparison of metal concentrations measured in <500 μm sediments in 2011 by Hill Laboratories and by University of Waikato.

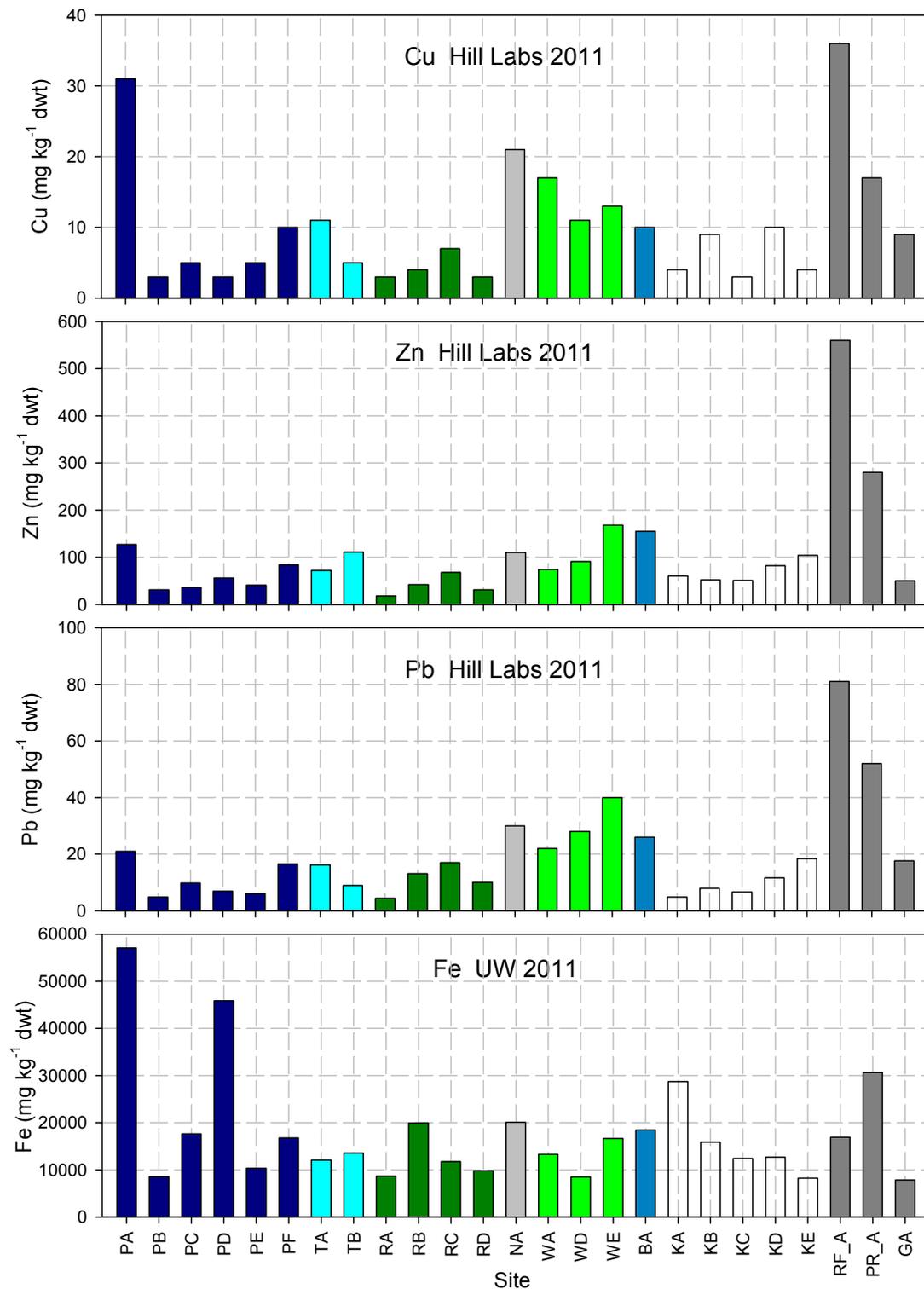


Figure A-2: Copper, zinc, lead and iron concentrations measured in <500 μm urban sediments in 2011 by Hill Laboratories or U. Waikato. Key to the site labels is provided in Table 2-1.

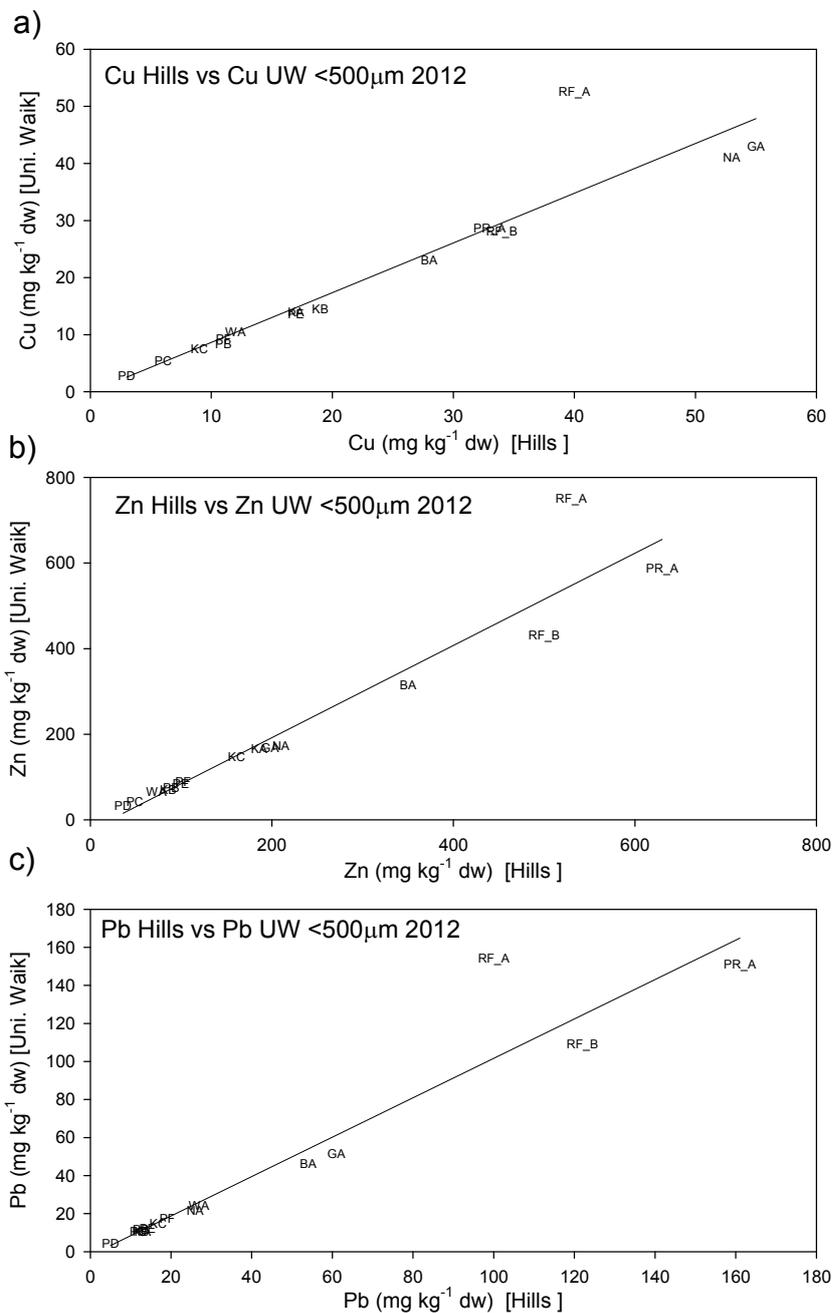


Figure A-3: Comparison of metal concentrations measured in the <500 μm sediments in 2012 by Hill laboratories and University of Waikato.

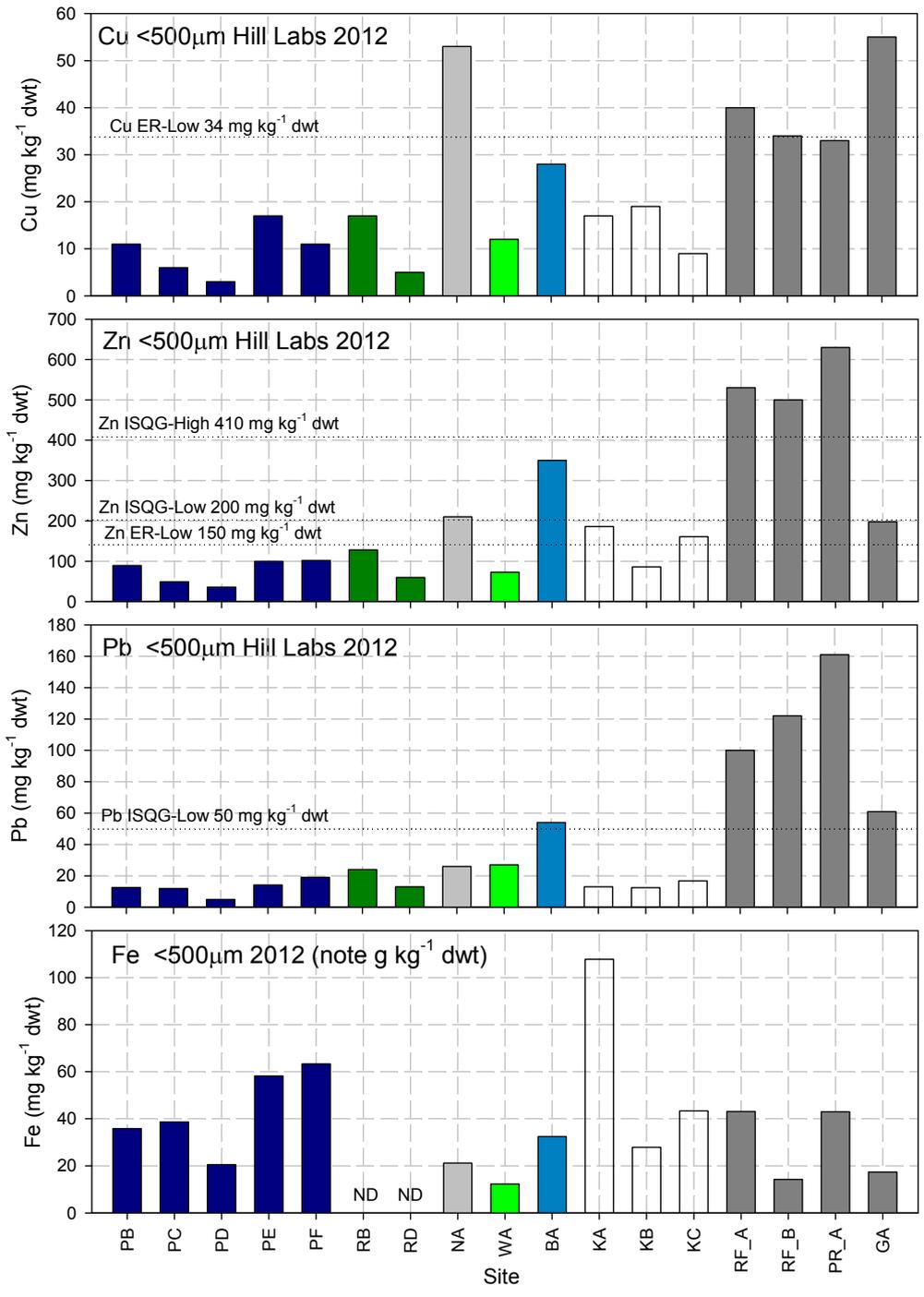


Figure A-4: Copper, zinc, and lead concentrations measured in <500 μm urban sediments in 2012 by Hill Laboratories. Iron was measured by University of Waikato. ND = no data.

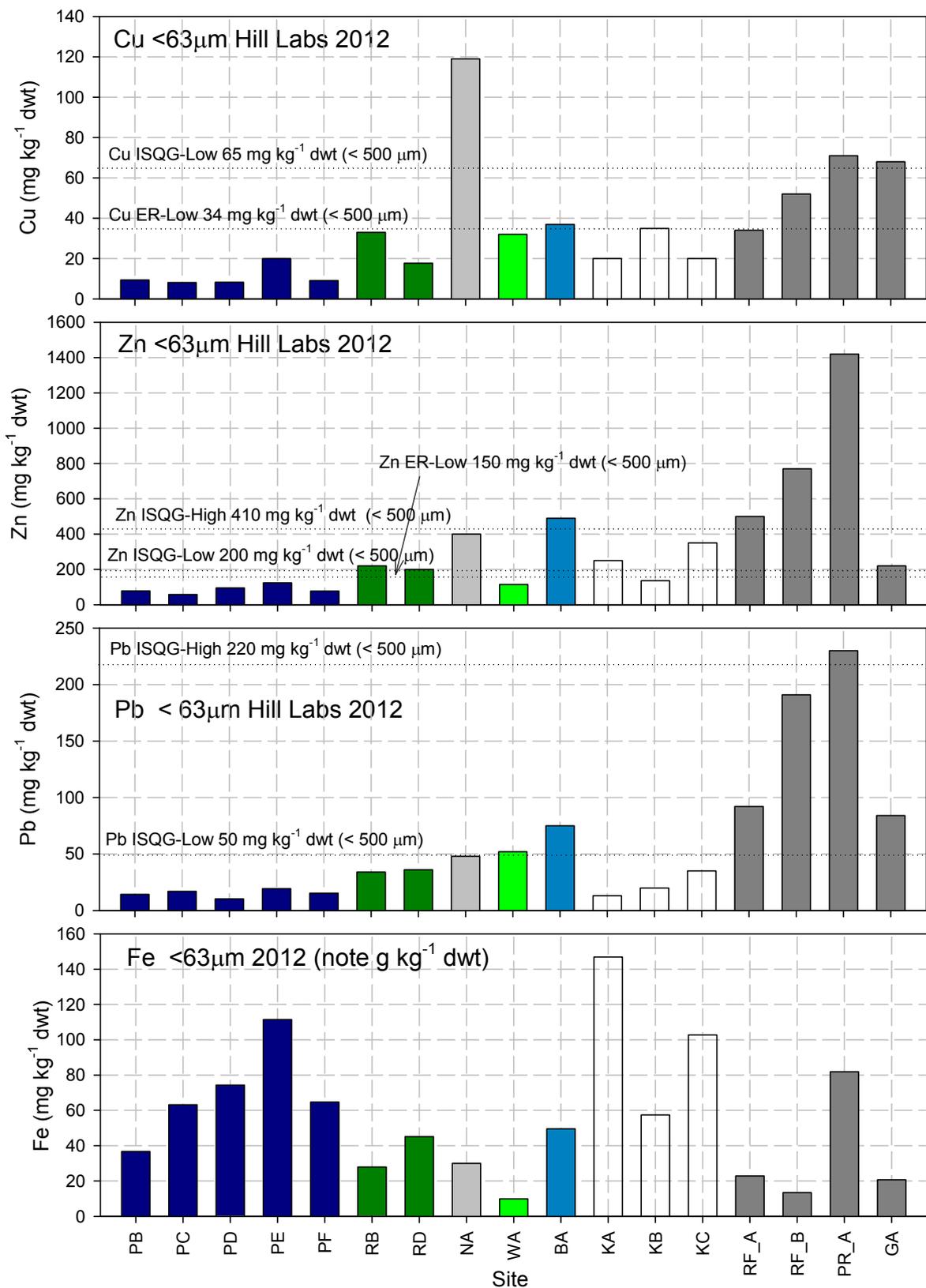


Figure A-5: Comparison of copper (Cu), zinc (Zn) and lead (Pb) concentrations measured in <63 μm sediments in 2012 by Hill laboratories and University of Waikato.

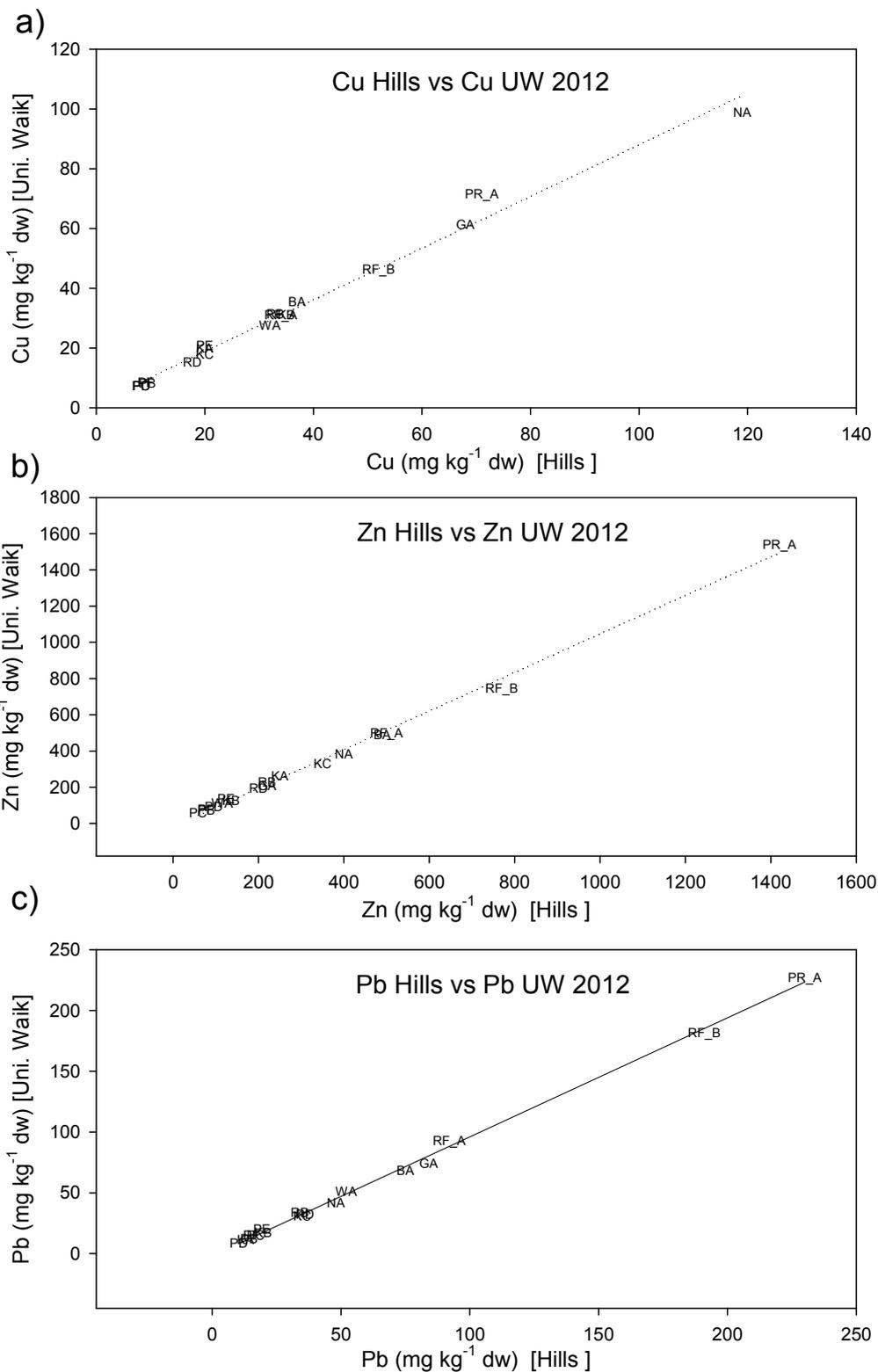


Figure A-6: Comparison of copper (Cu), zinc (Zn) and lead (Pb) concentrations measured in <63 μm sediments in 2012 by Hill laboratories and University of Waikato.

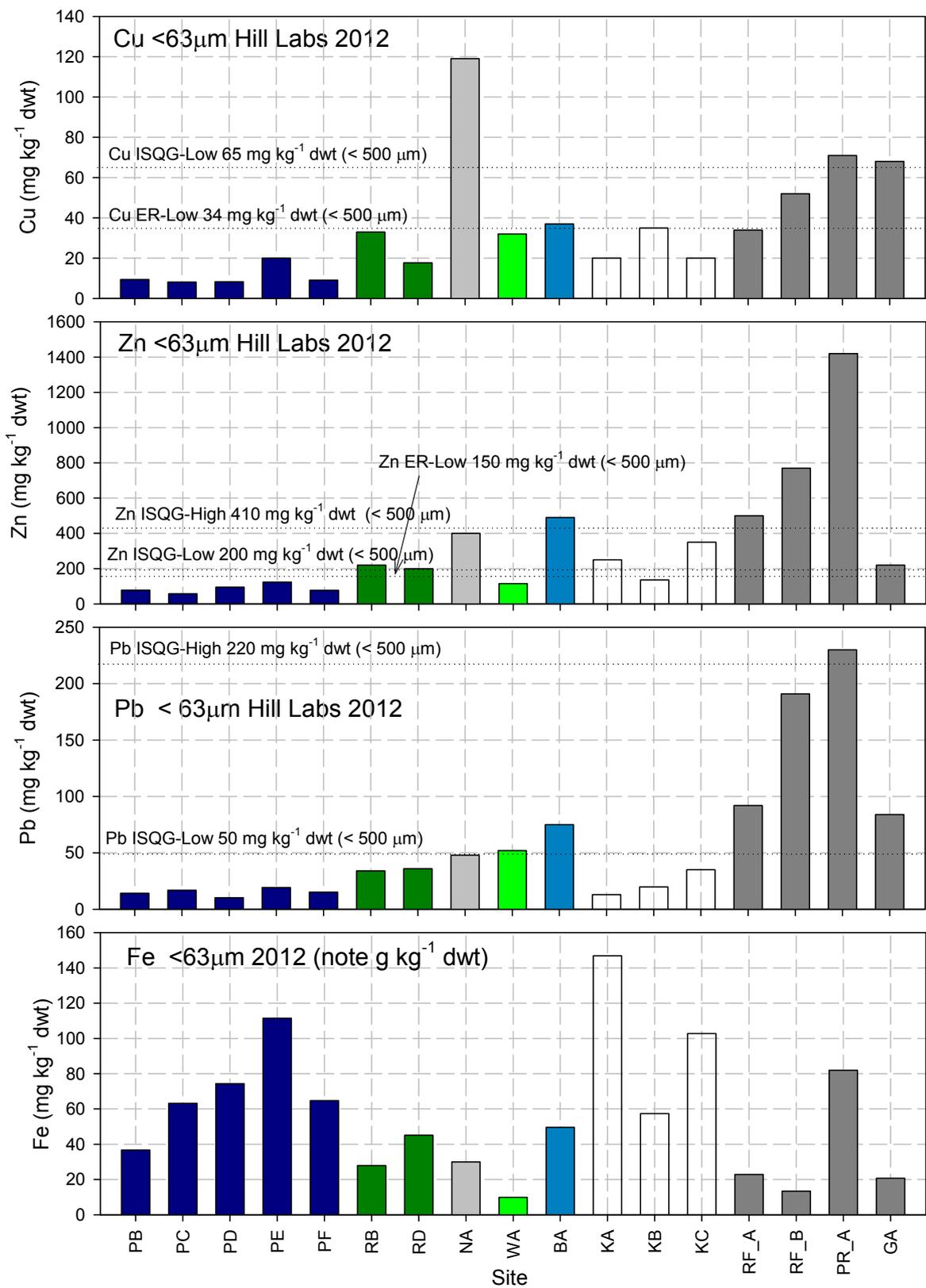


Figure A-7: Copper, zinc, and lead concentrations measured in <63 μm urban sediments in 2012 by Hill Laboratories. Iron was measured by University of Waikato.

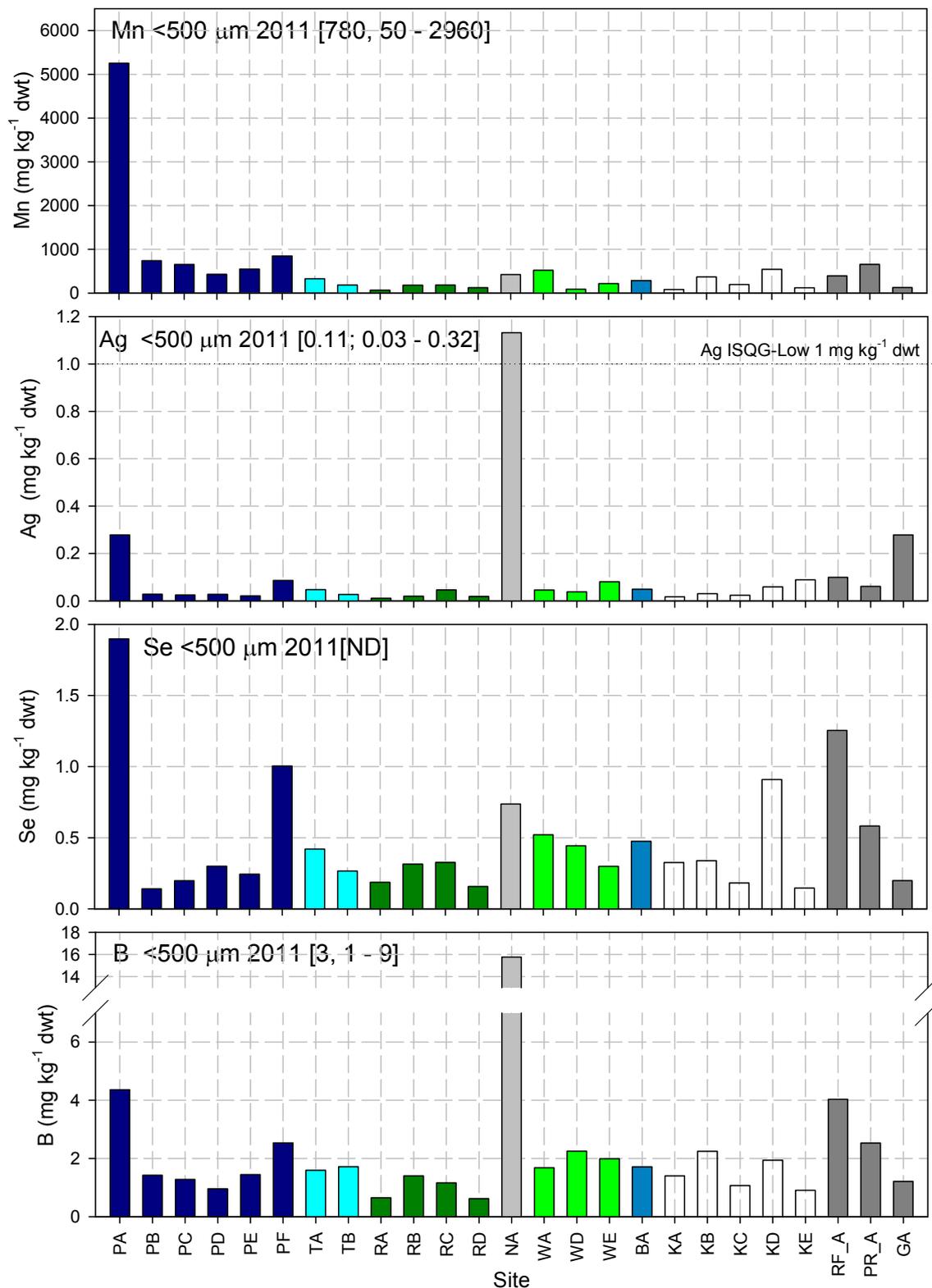


Figure A-8: Manganese (Mn), silver (Ag), selenium (Se) and boron (B) concentrations measured in <500 μm sediments in 2011. Key to site labels is provided in Table 2-1. Terrestrial soil background concentrations in square brackets (median, range).

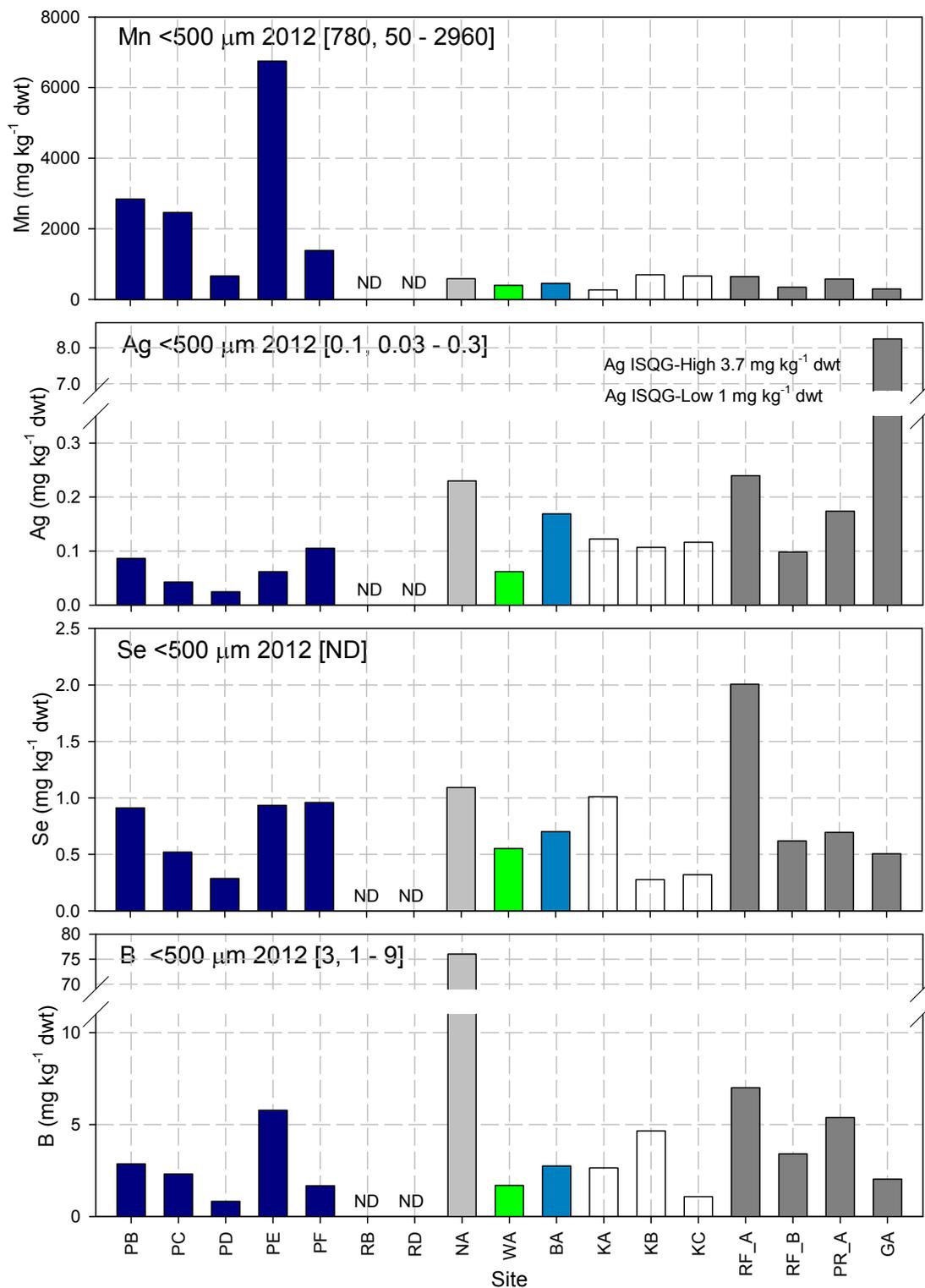


Figure A-9: Manganese (Mn), silver (Ag), selenium (Se) and boron (B) concentrations measured in <500 μm sediments in 2012. Key to site labels is provided in Table 2-1. Terrestrial soil background concentrations in square brackets (median, range). ND = no data.

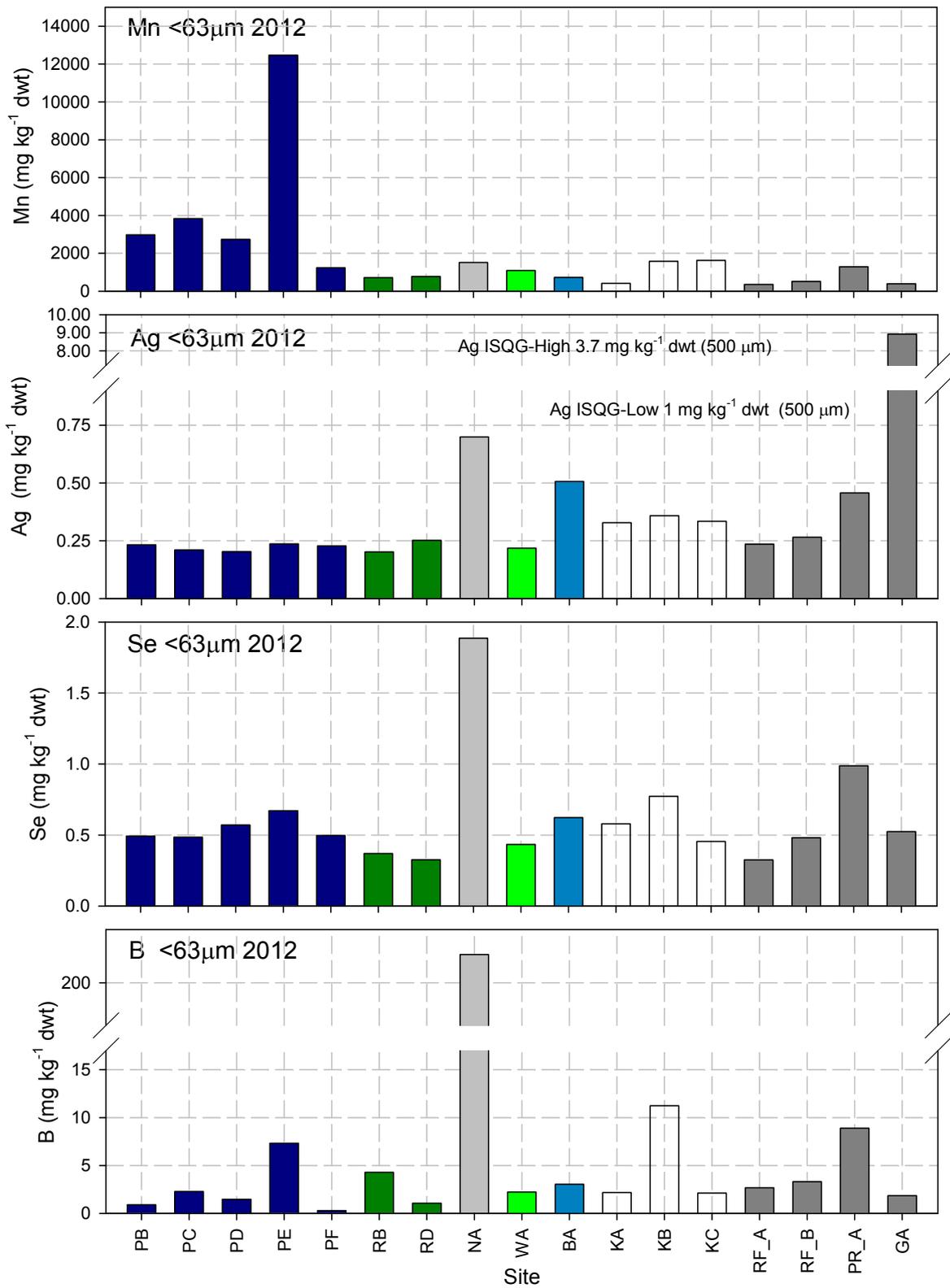


Figure A-10: Manganese (Mn), silver (Ag), selenium (Se) and boron (B) concentrations measured in Hamilton's <63 μm urban sediments in 2012. Key to site labels is provided in Table 2-1.

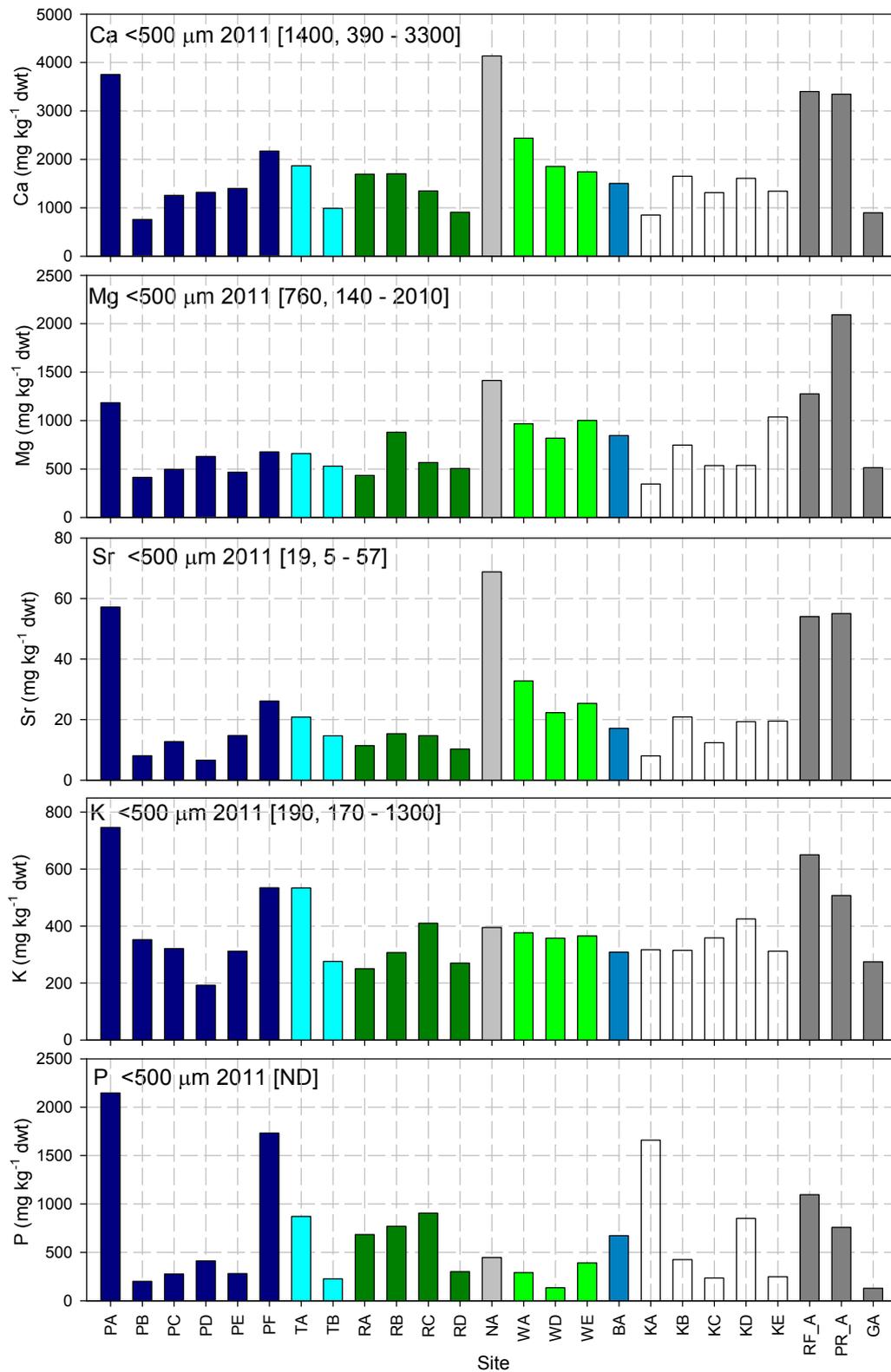


Figure A-11: Calcium (Ca), magnesium (Mg), strontium (Sr) potassium (K) and phosphorus (P) concentrations in <500 μm sediments in 2011. Key to site labels is provided in Table 2-1. Terrestrial soil background concentrations in square brackets (median, range). ND = no data.

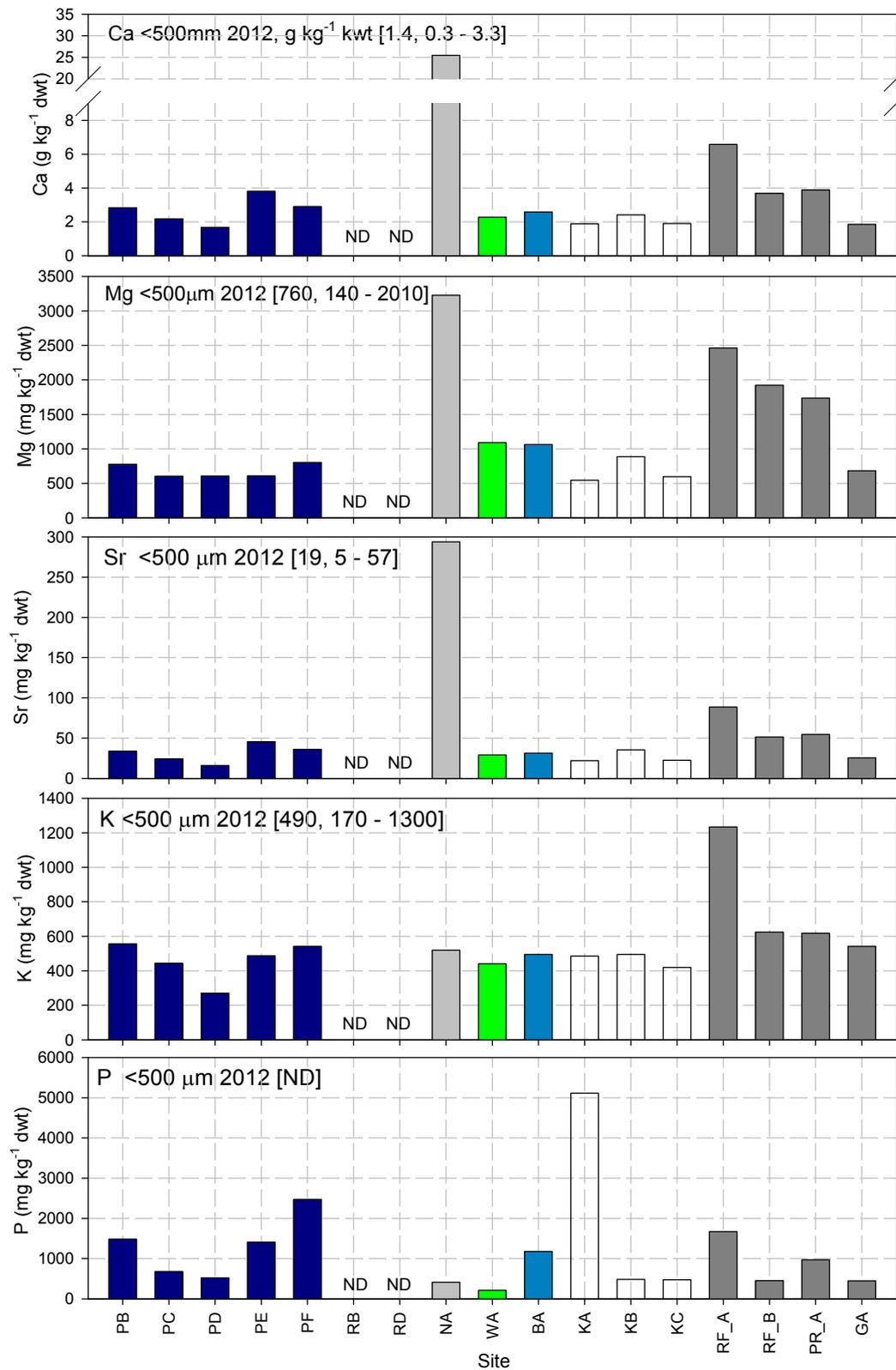


Figure A-12: Calcium (Ca), magnesium (Mg), strontium (Sr) potassium (K) and phosphorus (P) concentrations in <500 μm sediments in 2012. Key to site labels is provided in Table 2-1. Terrestrial soil background concentrations in square brackets (median, range). ND = no data.

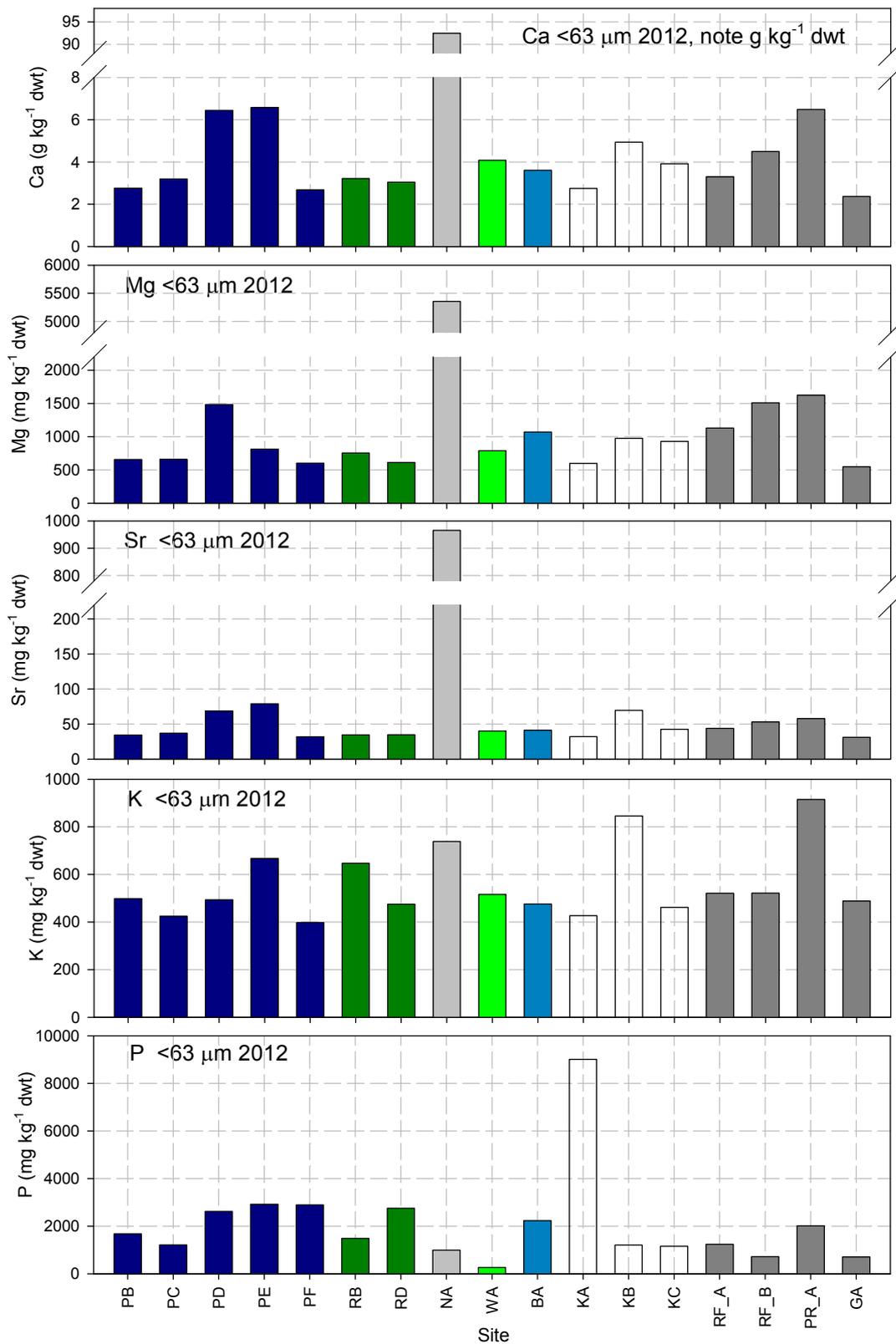


Figure A-13: Calcium (Ca), magnesium (Mg), strontium (Sr) potassium (K) and phosphorus (P) concentrations in <63 μm sediments in 2012. Key to site labels is provided in Table 2-1.

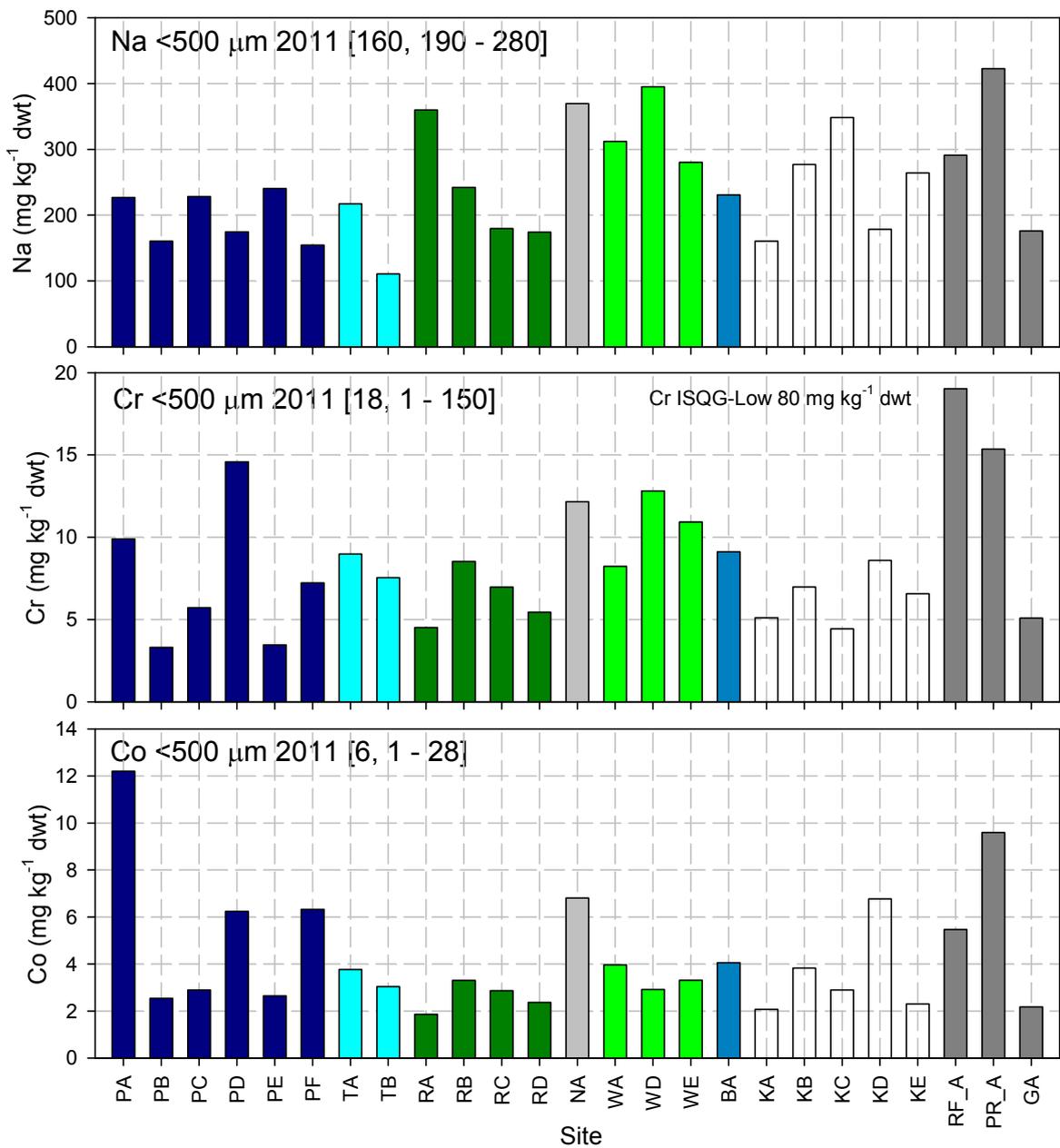


Figure A-14: Sodium (Na), chromium (Cr) and cobalt (Co) concentrations in <500 μm sediments in 2011. Key to site labels is provided in Table 2-1. Terrestrial soil background concentrations in square brackets (median, range).

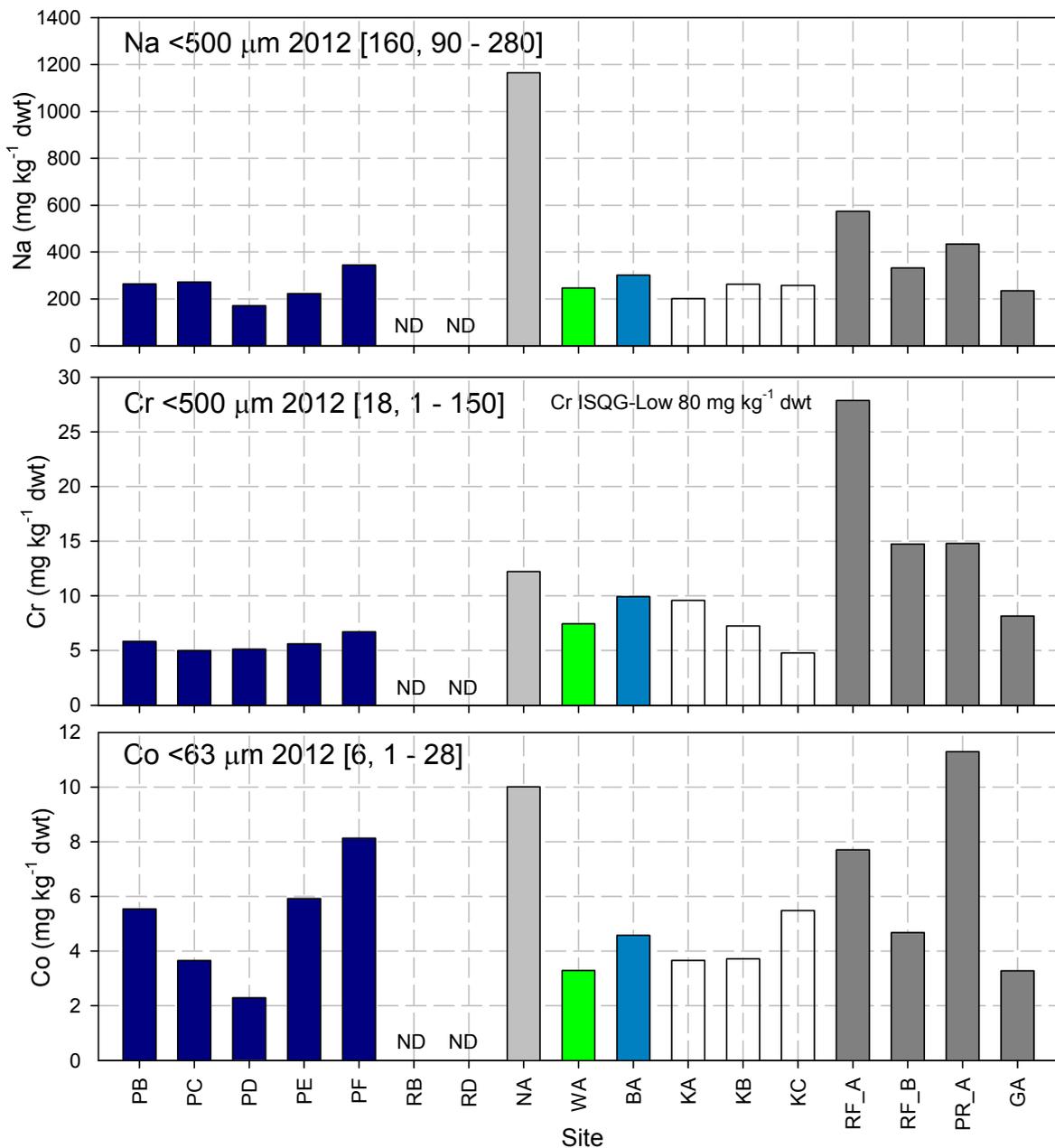


Figure A-15: Sodium (Na), chromium (Cr) and cobalt (Co) concentrations in <500 μm sediments in 2012. Key to site labels is provided in Table 2-1. Terrestrial soil background concentrations in square brackets (median, range), ND = no data.

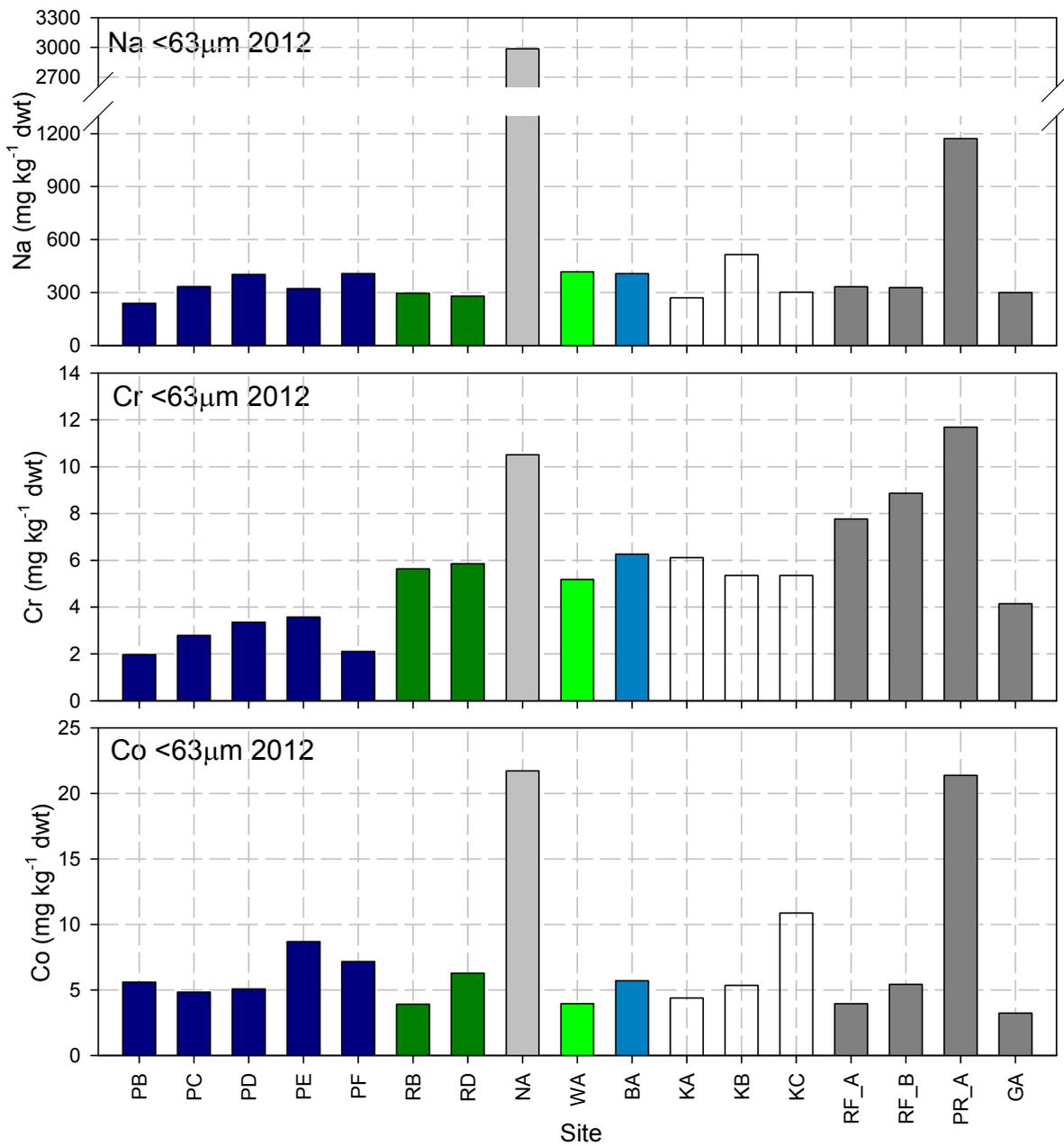


Figure A-16: Sodium (Na), chromium (Cr) and cobalt (Co) concentrations in <63 µm sediments in 2011. Key to site labels is provided in Table 2-1.

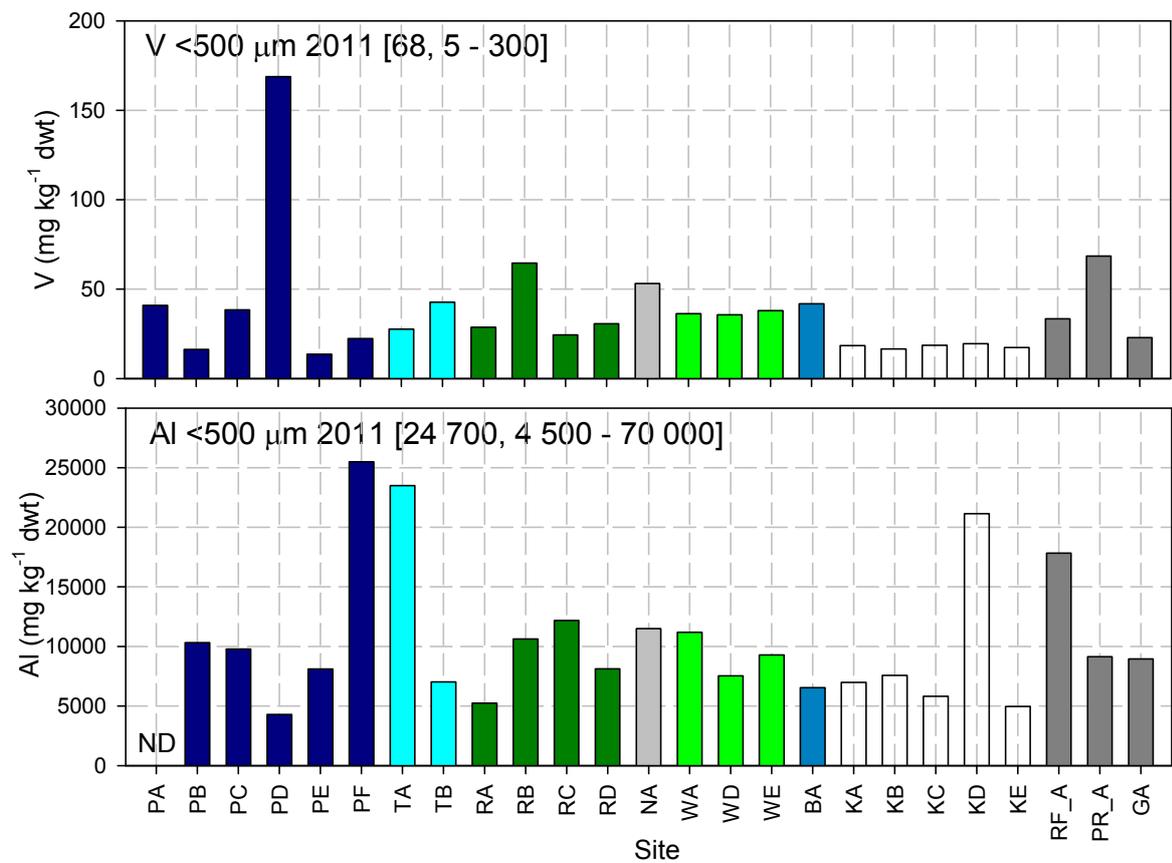


Figure A-17: Vanadium (V), and aluminium (Al) in <500 µm sediments in 2011. Thallium concentrations were not measured in 2011. Key to site labels is provided in Table 2-1. Terrestrial soil background concentrations in square brackets (median, range), ND = no data.

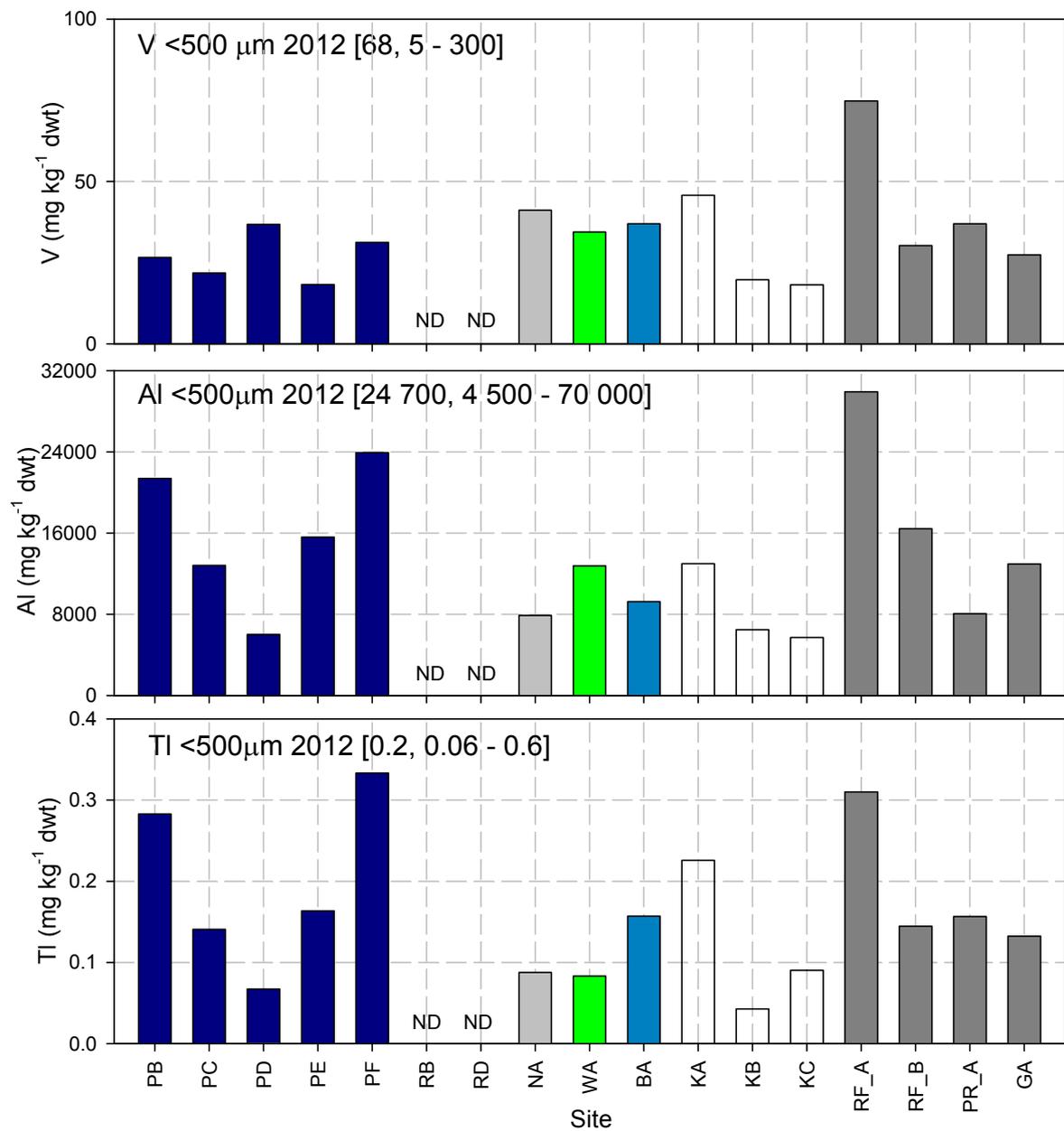


Figure A-18: Vanadium (V), aluminium (Al), and thallium (TI) concentrations in <500 μm sediments in 2012. Indium concentrations were not measured in 2012. Key to site labels is provided in Table 2-1. Terrestrial soil background concentrations in square brackets (median, range), ND = no data.

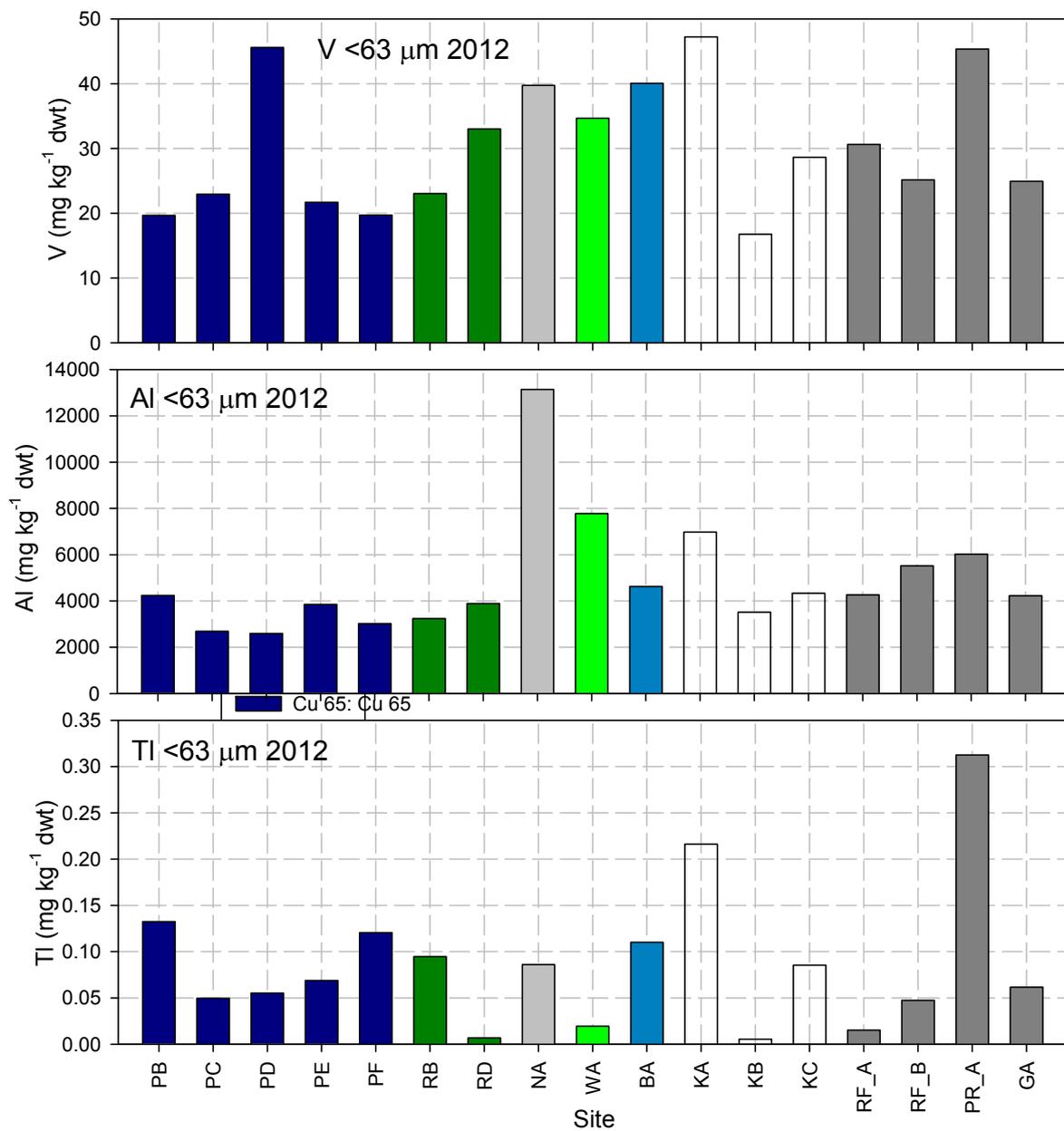


Figure A-19: Vanadium (V), aluminium (Al), and thallium (Tl) concentrations in <63 μm sediments in 2012. Indium concentrations were not measured in 2012. Key to site labels is provided in Table 2-1.

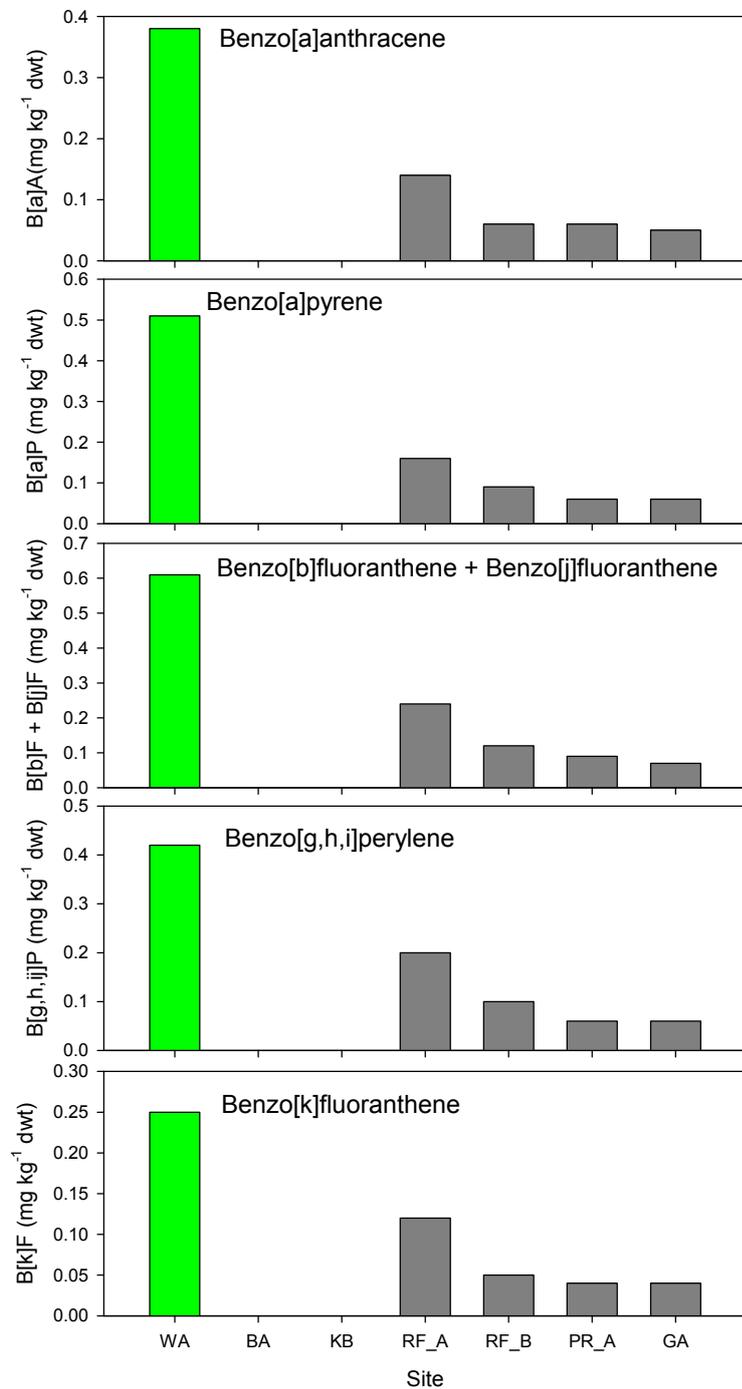


Figure A-20: Polycyclic aromatic hydrocarbon concentrations in urban sediments collected in 2012.

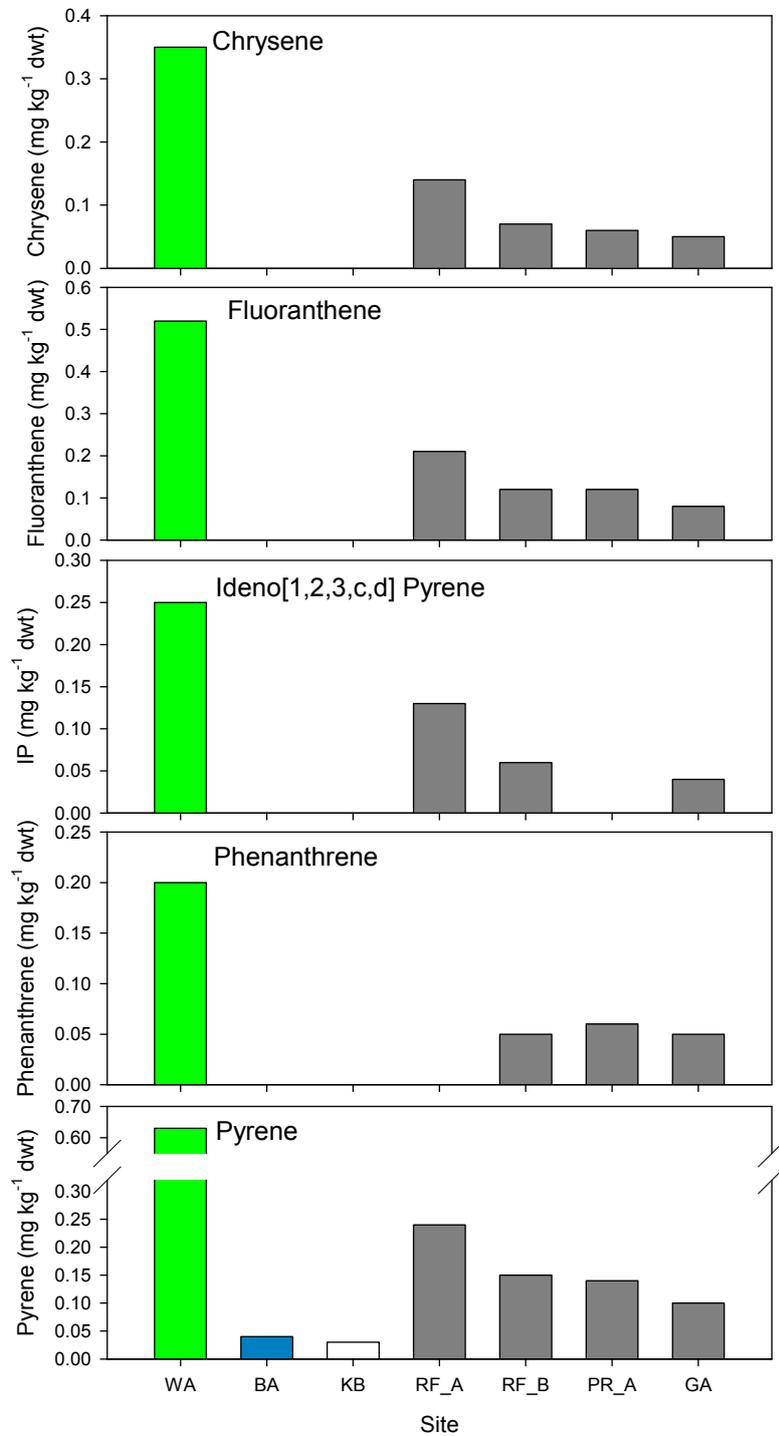


Figure A-21: Polycyclic aromatic hydrocarbon concentrations in urban sediments collected in 2012.

Appendix B Sediment metal concentrations

Table B-1: Metal and metalloid concentrations (mg kg⁻¹ dwt) in sediments from urban streams in Hamilton. Key to site labels in Table 2-1. Green, exceeds ER-L; orange exceeds ISQG-L; red, exceeds ISQG-H.

Site	Year	Sediment	Ag 109	Al 27	As 75	B 10	Ba 137	Ca 43	Cd 111	Co 59	Cr 52	Cu 65	Cu Hills	Fe 54	K 39	Mg 24
		Detection Limit	0.02	0.6	0.2	1.0	0.1	10	0.01	0.04	0.10	0.1	2	4	10	4
PA	2011	<500µm	0.28	HIGH	9.0	4.4	722	3752	0.48	12.2	9.9	27.1	31	57056	747	1185
PB	2011	<500µm	0.03	10323	2.3	1.4	90	760	0.05	2.5	3.3	3.2	3	8539	352	414
PC	2011	<500µm	0.02	9772	4.4	1.3	89	1256	0.04	2.9	5.7	4.9	5	17636	321	497
PD	2011	<500µm	0.03	4290	3.3	1.0	47	1320	0.05	6.2	14.6	4.7	3	45858	192	631
PE	2011	<500µm	0.02	8112	5.2	1.4	96	1400	0.06	2.6	3.5	5.0	5	10344	312	467
PF	2011	<500µm	0.09	25495	9.9	2.5	246	2173	0.72	6.3	7.2	10.3	10	16788	535	678
TA	2011	<500µm	0.05	23487	7.3	1.6	116	1867	0.09	3.8	9.0	11.2	11	12060	534	660
TB	2011	<500µm	0.03	7013	3.7	1.7	54	989	0.10	3.0	7.5	5.6	5	13586	276	530
RA	2011	<500µm	0.01	5243	3.2	0.6	32	1695	0.03	1.9	4.5	3.2	3	8664	250	433
RB	2011	<500µm	0.02	10632	4.1	1.4	55	1702	0.04	3.3	8.5	5.8	4	19959	307	881
RC	2011	<500µm	0.05	12177	6.6	1.2	77	1350	0.09	2.9	7.0	8.5	7	11777	410	567
RD	2011	<500µm	0.02	8117	2.6	0.6	41	907	0.03	2.4	5.4	3.7	3	9816	270	506
NA	2011	<500µm	1.13	11489	9.8	15.8	98	4134	0.13	6.8	12.2	23.0	21	20088	395	1415
WA	2011	<500µm	0.05	11187	62.7	1.7	78	2440	0.09	4.0	8.2	17.6	17	13298	377	967
WD	2011	<500µm	0.04	7534	4.0	2.3	52	1856	0.10	2.9	12.8	11.7	11	8484	357	818
WE	2011	<500µm	0.08	9279	8.9	2.0	66	1744	0.11	3.3	10.9	12.8	13	16677	365	1002
BA	2011	<500µm	0.05	6532	15.2	1.7	73	1502	0.21	4.1	9.1	11.8	10	18472	308	846
KA	2011	<500µm	0.02	6975	9.2	1.4	65	849	0.16	2.1	5.1	4.5	4	28711	317	345
KB	2011	<500µm	0.03	7578	18.7	2.2	113	1653	0.08	3.8	7.0	9.7	9	15886	314	748
KC	2011	<500µm	0.02	5813	9.3	1.1	52	1313	0.05	2.9	4.4	3.5	3	12423	358	535
KD	2011	<500µm	0.06	21147	13.3	1.9	155	1608	0.38	6.8	8.6	11.3	10	12701	425	536
KE	2011	<500µm	0.09	4971	7.0	0.9	39	1343	0.07	2.3	6.6	5.6	4	8262	312	1037
RF_A	2011	<500µm	0.10	17828	33.5	4.0	160	3401	0.51	5.5	19.0	35.7	36	16913	650	1277
PR_A	2011	<500µm	0.06	9135	17.8	2.5	99	3347	0.22	9.6	15.4	20.1	17	30642	507	2093
GA	2011	<500µm	0.28	8950	2.8	1.2	62	897	0.04	2.2	5.1	10.6	9	7849	274	513
		MEDIAN	0.05	9042.78	7.29	1.59	76.63	1608.07	0.09	3.30	7.54	9.74	9.00	13586.30	352.25	660.23

Table B-1 (continued).

Site	Year	Sediment	Ag 109	Al 27	As 75	B 10	Ba 137	Ca 43	Cd 111	Co 59	Cr 52	Cu 65	Cu Hills	Fe 54	K 39	Mg 24
PB	2012	<500µm	0.09	21382	10.7	2.9	412	2835	0.25	5.5	5.8	8.34	11	36	557	778
PC	2012	<500µm	0.04	12816	12.4	2.3	261	2177	0.10	3.7	5.0	5.34	6	39	444	606
PD	2012	<500µm	0.02	6001	3.9	0.8	123	1676	0.07	2.3	5.1	2.76	3	21	271	607
PE	2012	<500µm	0.06	15604	28.7	5.8	496	3818	0.23	5.9	5.6	13.70	17	58	487	609
PF	2012	<500µm	0.11	23936	15.3	1.7	440	2910	0.64	8.1	6.7	9.34	11	63	541	804
RB	2012		17	.	.	.
RD	2012		5	.	.	.
NA	2012	<500µm	0.23	7888	9.0	76.0	255	25438	0.06	10.0	12.2	41.11	53	21	519	3227
WA	2012	<500µm	0.06	12779	52.7	1.7	104	2278	0.08	3.3	7.4	10.48	12	12	441	1090
BA	2012	<500µm	0.17	9249	26.0	2.8	174	2583	0.31	4.6	9.9	23.01	28	32	495	1063
KA	2012	<500µm	0.12	12992	16.7	2.6	212	1888	0.49	3.7	9.6	13.91	17	108	485	544
KB	2012	<500µm	0.11	6481	24.3	4.7	263	2417	0.07	3.7	7.3	14.43	19	28	495	885
KC	2012	<500µm	0.12	5711	25.7	1.1	125	1903	0.12	5.5	4.8	7.54	9	43	420	598
RF_A	2012	<500µm	0.24	29913	53.8	7.0	353	6585	0.79	7.7	27.9	52.59	40	43	1234	2463
RF_B	2012	<500µm	0.10	16447	9.3	3.4	151	3684	0.32	4.7	14.7	28.05	34	14	625	1923
PR_A	2012	<500µm	0.17	8057	24.9	5.4	202	3886	0.40	11.3	14.8	28.57	33	43	618	1738
GA	2012	<500µm	8.25	12951	9.3	2.0	189	1860	0.14	3.3	8.2	42.94	55	17	542	684
		MEDIAN	0.11	12816.11	16.68	2.75	212.13	2582.71	0.23	4.68	7.44	13.91	17.00	35.84	495.33	804.44

Table B-1 (continued).

Site	Year	Sediment	Ag 109	Al 27	As 75	B 10	Ba 137	Ca 43	Cd 111	Co 59	Cr 52	Cu 65	Cu Hills	Fe 54	K 39	Mg 24
Detection Limit			0.05	1.5	0.5	2.5	0.25	25	0.03	0.10	0.25	0.25	1.00	10	25	10
PB	2012	<63µm	0.23	4238	8.0	0.9	422	2762	0.19	5.6	2.0	8.16	9.4	36694	498	656
PC	2012	<63µm	0.21	2690	14.8	2.3	393	3196	0.07	4.8	2.8	7.20	8.2	63234	425	658
PD	2012	<63µm	0.20	2600	15.1	1.5	490	6439	0.23	5.1	3.4	7.26	8.3	74311	494	1483
PE	2012	<63µm	0.24	3855	48.8	7.3	883	6580	0.25	8.7	3.6	20.76	20	111513	668	812
PF	2012	<63µm	0.23	3017	9.9	0.3	419	2689	0.49	7.2	2.1	8.62	9.1	64726	398	602
RK_B	2012	<63µm	0.20	3238	14.9	4.3	255	3212	0.46	3.9	5.6	31.33	33	27908	647	754
RK_D	2012	<63µm	0.25	3889	11.1	1.1	238	3041	0.15	6.3	5.9	15.24	17.7	45124	475	613
NA	2012	<63µm	0.70	13146	20.5	213.3	853	92472	0.39	21.7	10.5	98.95	119	29943	739	5356
WA	2012	<63µm	0.22	7778	69.8	2.2	264	4078	0.10	4.0	5.2	27.49	32	9848	516	790
BA	2012	<63µm	0.51	4625	37.4	3.0	272	3606	0.40	5.7	6.3	35.58	37	49548	476	1071
KA	2012	<63µm	0.33	6975	16.1	2.2	319	2750	0.68	4.4	6.1	19.84	20	146879	427	599
KB	2012	<63µm	0.36	3514	54.4	11.2	619	4939	0.13	5.3	5.4	31.18	35	57390	845	977
KC	2012	<63µm	0.34	4333	51.9	2.1	265	3919	0.29	10.9	5.3	18.00	20	102771	461	930
RF_A	2012	<63µm	0.24	4262	24.8	2.7	194	3300	0.33	4.0	7.8	31.14	34	22835	522	1132
RF_B	2012	<63µm	0.27	5517	8.7	3.3	232	4496	0.44	5.4	8.9	46.36	52	13402	522	1509
PR_A	2012	<63µm	0.46	6021	44.7	8.9	294	6484	1.03	21.4	11.7	71.56	71	81924	915	1623
GA	2012	<63µm	8.92	4225	8.1	1.8	274	2364	0.17	3.2	4.1	61.19	68	20752	488	550
		MEDIAN	0.25	4237.53	16.11	2.29	294.24	3606.15	0.29	5.43	5.35	27.49	32.00	49547.55	497.86	812.10

Table B-1 (continued).

Site	Year	Sediment	Mn 55	Na 23	Ni 60	P 31	Pb 207	Pb Hills	Se 82	Sr 88	Tl 205	V 51	Zn 66	Zn Hills
Detection Limit			0.1	4	0.2	4	0.04	0.4	0.2	0.1	0.01	0.4	0.2	4
PA	2011	<500µm	5253	227	4.5	2148	21	21	1.9	57	-	41	124	127
PB	2011	<500µm	741	161	1.6	201	4	5	0.1	8	-	16	28	31
PC	2011	<500µm	654	228	2.1	277	9	10	0.2	13	-	38	37	36
PD	2011	<500µm	429	175	3.0	413	6	7	0.3	7	-	169	87	56
PE	2011	<500µm	548	241	1.8	281	5	6	0.2	15	-	14	33	41
PF	2011	<500µm	847	155	3.2	1732	15	17	1.0	26	-	22	80	84
TA	2011	<500µm	328	217	6.6	872	13	16	0.4	21	-	28	67	72
TB	2011	<500µm	182	111	2.8	227	8	9	0.3	15	-	43	100	111
RA	2011	<500µm	64	360	2.1	684	4	4	0.2	11	-	29	20	18
RB	2011	<500µm	181	242	5.1	770	12	13	0.3	15	-	65	50	42
RC	2011	<500µm	185	180	3.3	906	15	17	0.3	15	-	24	59	68
RD	2011	<500µm	124	174	2.6	302	9	10	0.2	10	-	31	33	31
NA	2011	<500µm	424	369	9.8	446	27	30	0.7	69	-	53	99	110
WA	2011	<500µm	521	312	5.0	291	20	22	0.5	33	-	36	61	74
WD	2011	<500µm	89	395	5.6	135	25	28	0.4	22	-	36	80	91
WE	2011	<500µm	215	280	5.8	392	35	40	0.3	25	-	38	141	168
BA	2011	<500µm	284	231	5.0	674	23	26	0.5	17	-	42	133	155
KA	2011	<500µm	82	160	2.8	1659	4	5	0.3	8	-	18	50	60
KB	2011	<500µm	367	277	3.8	426	7	8	0.3	21	-	16	48	52
KC	2011	<500µm	196	348	2.5	236	6	7	0.2	12	-	19	49	51
KD	2011	<500µm	542	178	4.9	851	10	12	0.9	19	-	19	70	82
KE	2011	<500µm	119	264	5.2	249	16	18	0.1	19	-	17	87	104
RF_A	2011	<500µm	392	291	8.1	1096	70	81	1.3	54	-	33	436	560
PR_A	2011	<500µm	657	423	11.9	758	46	52	0.6	55	-	68	242	280
GA	2011	<500µm	127	176	2.6	129	16	18	0.2	ND	-	23	51	50
	2011.00	MEDIAN	328.15	230.61	3.80	426.32	13.36	16.20	0.33	18.23	-	30.57	66.58	72.00

Table B-1 (continued).

Site	Year	Sediment	Mn 55	Na 23	Ni 60	P 31	Pb 207	Pb Hills	Se 82	Sr 88	Tl 205	V 51	Zn 66	Zn Hills
PB	2012	<500µm	2843	264	2.7	1486	12	13	0.9	34	0.28	27	75	89
PC	2012	<500µm	2465	271	2.2	680	11	12	0.5	24	0.14	22	42	49
PD	2012	<500µm	662	171	1.6	522	4	5	0.3	16	0.07	37	34	36
PE	2012	<500µm	6750	223	2.5	1409	12	14	0.9	46	0.16	18	85	100
PF	2012	<500µm	1384	344	2.7	2473	18	19	1.0	36	0.33	31	90	102
	2012			24	128
	2012			13	60
NA	2012	<500µm	583	1165	18.5	414	22	26	1.1	294	0.09	41	172	210
WA	2012	<500µm	400	247	4.6	212	24	27	0.6	29	0.08	34	65	73
BA	2012	<500µm	455	301	5.4	1182	46	54	0.7	31	0.16	37	315	350
KA	2012	<500µm	267	201	4.3	5112	11	13	1.0	22	0.23	46	166	186
KB	2012	<500µm	696	263	3.3	486	10	13	0.3	35	0.04	20	71	86
KC	2012	<500µm	662	258	3.1	477	15	17	0.3	23	0.09	18	147	161
RF_A	2012	<500µm	645	574	11.2	1675	154	100	2.0	89	0.31	75	750	530
RF_B	2012	<500µm	346	332	7.9	456	109	122	0.6	51	0.14	30	432	500
PR_A	2012	<500µm	578	435	11.7	974	151	161	0.7	55	0.16	37	589	630
GA	2012	<500µm	292	235	3.7	449	52	61	0.5	25	0.13	27	169	198
		MEDIAN	645.26	264.04	3.74	680.22	17.60	19.10	0.70	33.79	0.14	31.23	146.60	128.00

Table B-1 (continued).

Site	Year	Sediment	Mn 55	Na 23	Ni 60	P 31	Pb 207	Pb Hills	Se 82	Sr 88	Tl 205	V 51	Zn 66	Zn Hills
Detection Limit			0.25	10	0.5	10	0.1	0.2	0.5	0.25	0.03	1.0	0.5	2.00
PB	2012	<63µm	2976	239	0.8	1677	12	14	0.5	34	0.13	20	75	78
PC	2012	<63µm	3835	333	1.0	1212	15	17	0.5	37	0.05	23	56	58
PD	2012	<63µm	2738	402	1.4	2620	9	10	0.6	69	0.06	46	92	95
PE	2012	<63µm	12464	322	1.5	2921	20	19	0.7	79	0.07	22	134	124
PF	2012	<63µm	1238	407	0.9	2896	15	15	0.5	32	0.12	20	78	77
RK_B	2012	<63µm	718	295	3.1	1485	33	34	0.4	34	0.09	23	230	220
RK_D	2012	<63µm	775	279	3.1	2753	33	36	0.3	35	0.01	33	195	200
NA	2012	<63µm	1516	2985	31.7	994	41	48	1.9	966	0.09	40	383	400
WA	2012	<63µm	1087	417	2.9	264	51	52	0.4	40	0.02	35	112	115
BA	2012	<63µm	726	407	4.3	2233	69	75	0.6	41	0.11	40	490	490
KA	2012	<63µm	408	269	3.6	9006	12	13	0.6	32	0.22	47	262	250
KB	2012	<63µm	1578	515	3.0	1204	17	20	0.8	70	0.01	17	125	136
KC	2012	<63µm	1627	302	4.8	1154	31	35	0.5	43	0.09	29	330	350
RF_A	2012	<63µm	358	332	4.3	1241	93	92	0.3	44	0.02	31	499	500
RF_B	2012	<63µm	514	327	5.8	718	182	191	0.5	53	0.05	25	748	770
PR_A	2012	<63µm	1288	1172	15.9	2011	227	230	1.0	58	0.31	45	1539	1,420
GA	2012	<63µm	392	300	2.2	708	74	84	0.5	31	0.06	25	210	220
		MEDIAN	1237.69	331.75	3.10	1484.76	32.64	35.00	0.50	41.12	0.07	28.63	210.40	220.00

Table B-2: Ratio of element concentration at site compared to median value for all sites. Key to site labels is in Table 2-1.

Site	Year	Sediment	Ag 109	Al 27	As 75	B 10	Ba 137	Ca 43	Cd 111	Co 59	Cr 52	Cu 65	Cu Hills	Fe 54	K 39	Mg 24
Detection Limit			0.02	0.6	0.2	1.0	0.1	10	0.01	0.04	0.10	0.1	2	4	10	4
PA	2011	<500µm	6	-	1	3	9	2	5	4	1	3	3	4	2	2
PB	2011	<500µm	1	1	0	1	1	0	1	1	0	0	0	1	1	1
PC	2011	<500µm	1	1	1	1	1	1	0	1	1	1	1	1	1	1
PD	2011	<500µm	1	0	0	1	1	1	0	2	2	0	0	3	1	1
PE	2011	<500µm	0	1	1	1	1	1	1	1	0	1	1	1	1	1
PF	2011	<500µm	2	3	1	2	3	1	8	2	1	1	1	1	2	1
TA	2011	<500µm	1	3	1	1	2	1	1	1	1	1	1	1	2	1
TB	2011	<500µm	1	1	1	1	1	1	1	1	1	1	1	1	1	1
RA	2011	<500µm	0	1	0	0	0	1	0	1	1	0	0	1	1	1
RB	2011	<500µm	0	1	1	1	1	1	0	1	1	1	0	1	1	1
RC	2011	<500µm	1	1	1	1	1	1	1	1	1	1	1	1	1	1
RD	2011	<500µm	0	1	0	0	1	1	0	1	1	0	0	1	1	1
NA	2011	<500µm	24	1	1	10	1	3	1	2	2	2	2	1	1	2
WA	2011	<500µm	1	1	9	1	1	2	1	1	1	2	2	1	1	1
WD	2011	<500µm	1	1	1	1	1	1	1	1	2	1	1	1	1	1
WE	2011	<500µm	2	1	1	1	1	1	1	1	1	1	1	1	1	2
BA	2011	<500µm	1	1	2	1	1	1	2	1	1	1	1	1	1	1
KA	2011	<500µm	0	1	1	1	1	1	2	1	1	0	0	2	1	1
KB	2011	<500µm	1	1	3	1	1	1	1	1	1	1	1	1	1	1
KC	2011	<500µm	1	1	1	1	1	1	1	1	1	0	0	1	1	1
KD	2011	<500µm	1	2	2	1	2	1	4	2	1	1	1	1	1	1
KE	2011	<500µm	2	1	1	1	1	1	1	1	1	1	0	1	1	2
RF_A	2011	<500µm	2	2	5	3	2	2	5	2	3	4	4	1	2	2
PR_A	2011	<500µm	1	1	2	2	1	2	2	3	2	2	2	2	1	3
GA	2011	<500µm	6	1	0	1	1	1	0	1	1	1	1	1	1	1

Table B-2 (continued).

Site	Year	Sediment	Ag 109	Al 27	As 75	B 10	Ba 137	Ca 43	Cd 111	Co 59	Cr 52	Cu 65	Cu Hills	Fe 54	K 39	Mg 24
PB	2012	<500µm	1	2	1	1	2	1	1	1	1	1	1	1	1	1
PC	2012	<500µm	0	1	1	1	1	1	0	1	1	0	0	1	1	1
PD	2012	<500µm	0	0	0	0	1	1	0	0	1	0	0	1	1	1
PE	2012	<500µm	1	1	2	2	2	1	1	1	1	1	1	2	1	1
PF	2012	<500µm	1	2	1	1	2	1	3	2	1	1	1	2	1	1
RB	2012		-	-	-	-	-	-	-	-	-	-	1	-	-	-
RD	2012		-	-	-	-	-	-	-	-	-	-	0	-	-	-
NA	2012	<500µm	2	1	1	28	1	10	0	2	2	3	3	1	1	4
WA	2012	<500µm	1	1	3	1	0	1	0	1	1	1	1	0	1	1
BA	2012	<500µm	2	1	2	1	1	1	1	1	1	2	2	1	1	1
KA	2012	<500µm	1	1	1	1	1	1	2	1	1	1	1	3	1	1
KB	2012	<500µm	1	1	1	2	1	1	0	1	1	1	1	1	1	1
KC	2012	<500µm	1	0	2	0	1	1	1	1	1	1	1	1	1	1
RF_A	2012	<500µm	2	2	3	3	2	3	3	2	4	4	2	1	2	3
RF_B	2012	<500µm	1	1	1	1	1	1	1	1	2	2	2	0	1	2
PR_A	2012	<500µm	2	1	1	2	1	2	2	2	2	2	2	1	1	2
GA	2012	<500µm	77	1	1	1	1	1	1	1	1	3	3	0	1	1

Table B-2 (continued).

Site	Year	Sediment	Ag 109	Al 27	As 75	B 10	Ba 137	Ca 43	Cd 111	Co 59	Cr 52	Cu 65	Cu Hills	Fe 54	K 39	Mg 24
Detection Limit			0	2	1	3	0	25	0	0	0	0	1	10	25	10
PB	2012	<63µm	1	1	0	0	1	1	1	1	0	0	0	1	1	1
PC	2012	<63µm	1	1	1	1	1	1	0	1	1	0	0	1	1	1
PD	2012	<63µm	1	1	1	1	2	2	1	1	1	0	0	1	1	2
PE	2012	<63µm	1	1	3	3	3	2	1	2	1	1	1	2	1	1
PF	2012	<63µm	1	1	1	0	1	1	2	1	0	0	0	1	1	1
RK_B	2012	<63µm	1	1	1	2	1	1	2	1	1	1	1	1	1	1
RK_D	2012	<63µm	1	1	1	0	1	1	1	1	1	1	1	1	1	1
NA	2012	<63µm	3	3	1	93	3	26	1	4	2	4	4	1	1	7
WA	2012	<63µm	1	2	4	1	1	1	0	1	1	1	1	0	1	1
BA	2012	<63µm	2	1	2	1	1	1	1	1	1	1	1	1	1	1
KA	2012	<63µm	1	2	1	1	1	1	2	1	1	1	1	3	1	1
KB	2012	<63µm	1	1	3	5	2	1	0	1	1	1	1	1	2	1
KC	2012	<63µm	1	1	3	1	1	1	1	2	1	1	1	2	1	1
RF_A	2012	<63µm	1	1	2	1	1	1	1	1	1	1	1	0	1	1
RF_B	2012	<63µm	1	1	1	1	1	1	1	1	2	2	2	0	1	2
PR_A	2012	<63µm	2	1	3	4	1	2	4	4	2	3	2	2	2	2
GA	2012	<63µm	35	1	1	1	1	1	1	1	1	2	2	0	1	1

Table B-2 (continued).

Site	Year	Sediment	Mn 55	Na 23	Ni 60	P 31	Pb 207	Pb Hills	Se 82	Sr 88	Tl 205	V 51	Zn 66	Zn Hills
Detection Limit		Detection	0.1	4	0.2	4	0.04	0.4	0.2	0.1	0.01	0.4	0.2	4
PA	2011	<500µm	16	1	1	5	2	1	6	3	-	1	2	2
PB	2011	<500µm	2	1	0	0	0	0	0	0	-	1	0	0
PC	2011	<500µm	2	1	1	1	1	1	1	1	-	1	1	1
PD	2011	<500µm	1	1	1	1	0	0	1	0	-	6	1	1
PE	2011	<500µm	2	1	0	1	0	0	1	1	-	0	0	1
PF	2011	<500µm	3	1	1	4	1	1	3	1	-	1	1	1
TA	2011	<500µm	1	1	2	2	1	1	1	1	-	1	1	1
TB	2011	<500µm	1	0	1	1	1	1	1	1	-	1	1	2
RA	2011	<500µm	0	2	1	2	0	0	1	1	-	1	0	0
RB	2011	<500µm	1	1	1	2	1	1	1	1	-	2	1	1
RC	2011	<500µm	1	1	1	2	1	1	1	1	-	1	1	1
RD	2011	<500µm	0	1	1	1	1	1	0	1	-	1	1	0
NA	2011	<500µm	1	2	3	1	2	2	2	4	-	2	1	2
WA	2011	<500µm	2	1	1	1	1	1	2	2	-	1	1	1
WD	2011	<500µm	0	2	1	0	2	2	1	1	-	1	1	1
WE	2011	<500µm	1	1	2	1	3	2	1	1	-	1	2	2
BA	2011	<500µm	1	1	1	2	2	2	1	1	-	1	2	2
KA	2011	<500µm	0	1	1	4	0	0	1	0	-	1	1	1
KB	2011	<500µm	1	1	1	1	0	0	1	1	-	1	1	1
KC	2011	<500µm	1	2	1	1	0	0	1	1	-	1	1	1
KD	2011	<500µm	2	1	1	2	1	1	3	1	-	1	1	1
KE	2011	<500µm	0	1	1	1	1	1	0	1	-	1	1	1
RF_A	2011	<500µm	1	1	2	3	5	5	4	3	-	1	7	8
PR_A	2011	<500µm	2	2	3	2	3	3	2	3	-	2	4	4
GA	2011	<500µm	0	1	1	0	1	1	1	-	-	1	1	1

Table B-2 (continued).

Site	Year	Sediment	Mn 55	Na 23	Ni 60	P 31	Pb 207	Pb Hills	Se 82	Sr 88	Tl 205	V 51	Zn 66	Zn Hills
PB	2012	<500µm	4	1	1	2	1	1	1	1	2	1	1	1
PC	2012	<500µm	4	1	1	1	1	1	1	1	1	1	0	0
PD	2012	<500µm	1	1	0	1	0	0	0	0	0	1	0	0
PE	2012	<500µm	10	1	1	2	1	1	1	1	1	1	1	1
PF	2012	<500µm	2	1	1	4	1	1	1	1	2	1	1	1
	2012		-	-	-	-	-	1	-	-	-	-	-	1
	2012		-	-	-	-	-	1	-	-	-	-	-	0
NA	2012	<500µm	1	4	5	1	1	1	2	9	1	1	1	2
WA	2012	<500µm	1	1	1	0	1	1	1	1	1	1	0	1
BA	2012	<500µm	1	1	1	2	3	3	1	1	1	1	2	3
KA	2012	<500µm	0	1	1	8	1	1	1	1	2	1	1	1
KB	2012	<500µm	1	1	1	1	1	1	0	1	0	1	0	1
KC	2012	<500µm	1	1	1	1	1	1	0	1	1	1	1	1
RF_A	2012	<500µm	1	2	3	2	9	5	3	3	2	2	5	4
RF_B	2012	<500µm	1	1	2	1	6	5	1	2	1	1	3	4
PR_A	2012	<500µm	1	2	3	1	9	8	1	2	1	1	4	5
GA	2012	<500µm	0	1	1	1	3	3	1	1	1	1	1	2

Table B-2 (continued).

Site	Year	Sediment	Mn 55	Na 23	Ni 60	P 31	Pb 207	Pb Hills	Se 82	Sr 88	Tl 205	V 51	Zn 66	Zn Hills
Detection Limit			0.25	10	0.5	10	0.1	0.2	0.5	0.25	0.03	1.0	0.5	2.00
PB	2012	<63µm	2	1	0	1	0	0	1	1	2	1	0	0
PC	2012	<63µm	3	1	0	1	0	0	1	1	1	1	0	0
PD	2012	<63µm	2	1	0	2	0	0	1	2	1	2	0	0
PE	2012	<63µm	10	1	0	2	1	1	1	2	1	1	1	1
PF	2012	<63µm	1	1	0	2	0	0	1	1	2	1	0	0
RK_B	2012	<63µm	1	1	1	1	1	1	1	1	1	1	1	1
RK_D	2012	<63µm	1	1	1	2	1	1	1	1	0	1	1	1
NA	2012	<63µm	1	9	10	1	1	1	4	23	1	1	2	2
WA	2012	<63µm	1	1	1	0	2	1	1	1	0	1	1	1
BA	2012	<63µm	1	1	1	2	2	2	1	1	2	1	2	2
KA	2012	<63µm	0	1	1	6	0	0	1	1	3	2	1	1
KB	2012	<63µm	1	2	1	1	1	1	2	2	0	1	1	1
KC	2012	<63µm	1	1	2	1	1	1	1	1	1	1	2	2
RF_A	2012	<63µm	0	1	1	1	3	3	1	1	0	1	2	2
RF_B	2012	<63µm	0	1	2	0	6	5	1	1	1	1	4	4
PR_A	2012	<63µm	1	4	5	1	7	7	2	1	5	2	7	6
GA	2012	<63µm	0	1	1	0	2	2	1	1	1	1	1	1

Appendix C Amphipod Test Conditions Summary

Parameter	Conditions
Test species	<i>Chaetocorophium cf lucasi</i>
Test organisms	>500 µm <i>C. lucasi</i> , 20 per replicate
Test organism source	Lake Rotorua littoral zone by confluence with Hamurana spring
Test type	Acute, static, 10-day duration
Replicates	Three per treatment, six control replicates (Lake Rotorua sediments)
Test vessel	680 mL polypropylene jars, pre-soaked in freshwater
Control sediment	<500 µm sediment from Lake Rotorua collection site, equilibrated for 5 days after sieving
Reference sediment	Clean sediment, with similar particle size distribution and organic matter content as the other test sediments. Refer to control sediment in this test as composition similar to test sediments.
Test water	Dechlorinated Hamilton City Tap Water
Temperature	15°C
Salinity	0 ppt
Lighting	16:8 light:dark photoperiod
Feeding	None
Aeration	Gentle aeration of overlying water with 1 whisker/jar (<100 bubbles/minute), prior to adding amphipods.
Observations	Daily observation, counting and removal of mortalities, checking aeration. Every 2 or 3 days, check dissolved oxygen, pH, conductivity and temperature in 1 replicate of each treatment. Check all parameters if large numbers of mortalities in one treatment or replicate.
Endpoints	Mortality and reburial (optional).
Test validity	Invalid if overall mortalities in control treatment are >10%, or if >20% mortality occurs in any of the control replicates. Invalid if sensitivity of test organisms to reference toxicant is out of the normal range.