### CITY OF WHITTLESEA STORMWATER QUALITY MONITORING PROGRAM

Stephen Marshall, environmental scientist, freshwater group; capim Voytek Lapinski, environmental infrastructure officer, city of whittlesea

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### VICTORIAN CENTRE FOR AQUATIC POLLUTION IDENTIFICATION AND MANAGEMENT TECHNICAL REPORT #05: CITY OF WHITTLESEA STORMWATER QUALITY MONITORING PROGRAM

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### **Executive Summary**

The City of Whittlesea commissioned the Victorian Centre for Aquatic Pollution Investigation and Management (CAPIM) to assess the relative contribution of residential and industrial catchments to non-point source pollution in and around Edgar's Creek. A survey of heavy metal and hydrocarbon contamination of the stormwater drainage network found industrial estates were clearly associated with higher pollutant loads. Passive sampling surveys of the subterranean stormwater drainage network found four sub-catchments with consistently high levels of pollution. These areas were referred to EPA Victoria for further investigation. In conclusion, industrial estates are clearly a high priority for stormwater education programs, and a follow-up survey of stormwater quality is strongly recommended to assess the programs' impact in reducing pollution.

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### Introduction

Stormwater is the major source of pollution to urban waterways (Pettigrove et al., 2003c), and poor stormwater management practices in industrial catchments are thought to be a major contributor (Pettigrove et al., 2003b). Therefore, improving stormwater quality typically requires changing business work habits throughout the catchment. In spite of the perceived difficulty of changing human behavior, recent work in this area has been encouraging.

Local councils can improve work habits in small industrial areas, producing measurable reductions in stormwater pollution (Barrett et al., 2008; Marshall et al., 2008a). Site inspections of Melbourne businesses by regulatory authorities have led to measurable and lasting improvements in work practices relevant to stormwater management (Barrett et al., 2008; BMT WBM Pty Ltd, 2009). When re-assessed after three years, businesses previously inspected by EPA Victoria were more aware of stormwater issues, were more likely to have correct trade waste arrangements, and were less likely to have visible signs of pollution around their stormwater drains (BMT WBM Pty Ltd, 2009). After twelve months, stormwater runoff from businesses inspected by City of Kingston industry stormwater teams was substantially cleaner than runoff from un-inspected businesses (Marshall et al., 2008a). These positive results show that substantial improvements in stormwater quality can be achieved through carefully targeted education and enforcement programs.

Stormwater quality in the Edgar's Creek catchment has been consistently poor for at least the last 20 years (Melbourne Water, unpublished data). Historically, the most common contaminants of concern have been heavy metals and hydrocarbons, although more exotic pollutants (eg: polychlorinated biphenyls (PCBs) and silver) have also been detected (Melbourne Water, unpublished data). Although stormwater management programs have proven effective in reducing stormwater pollution (Marshall et al., 2008a), they will be most cost-effective when targeted at the most heavily polluting sub-catchments. Therefore; council was particularly interested in establishing the significance of pollution from industrial areas in comparison to residential areas, to enable more effective targeting of stormwater management programs.

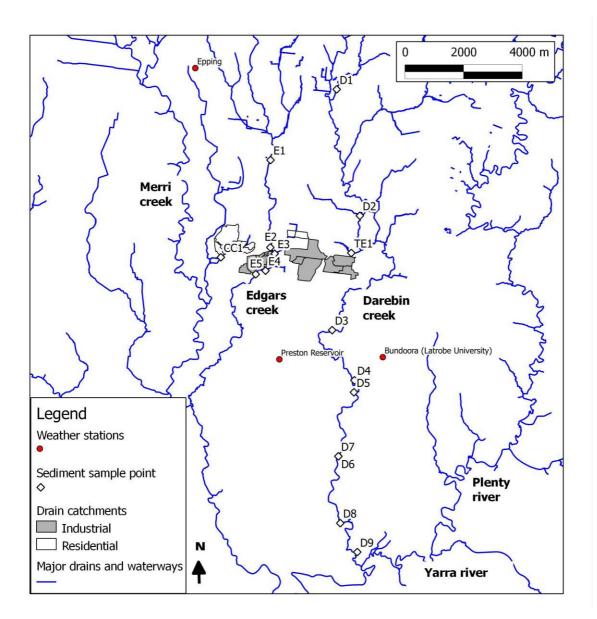
### **Study Objectives**

The primary aim of this survey was to directly compare stormwater quality from industrial and residential catchments. A secondary aim was to identify catchments producing consistently high pollution loads, as the premises in these areas are likely to be the focus of subsequent environmental education and improvement programs.

### **Materials and Methods**

### SURVEY LOCATIONS

The survey was conducted in a three stage process. In the first stage, existing sediment quality data along Darebin and Edgar's Creek was reviewed to identify pollution hotspots (Melbourne Water, 2007). To improve the spatial resolution of pollution transects the 2008 sediment quality survey of Edgar's Creek was repeated in 2010, with the addition of two more sites on Central Creek (CC1) and the Thomastown East Drain (TE1) (Fig 1).



# Figure 1. Sediment quality transect collection locations. Darebin Creek sites D1-D9 were surveyed in Spring 2006 and Autumn 2007. Edgar's Creek sites were surveyed in Spring 2008 and Spring 2010. Central Creek (CC1) and Thomastown East Drain (TE1) were surveyed in Spring 2010 only.

The second stage was a five-week pilot survey of pollutant loads in the stormwater drainage system immediately upstream of these hotspots. Pollutant loads were estimated using in-drain passive

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samplers; these consisted of polypropylene mesh bags containing 250mL of granular activated carbon (GAC) (Marshall et al., 2008b). Bags were secured in most cases by polypropylene cord (Fig 2a). Where no convenient attachment points were available, bags were attached to hook-and-loop fabric fastened to the drain wall via curved PVC mounting plates (Fig 2b).

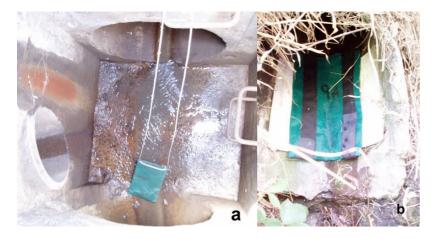
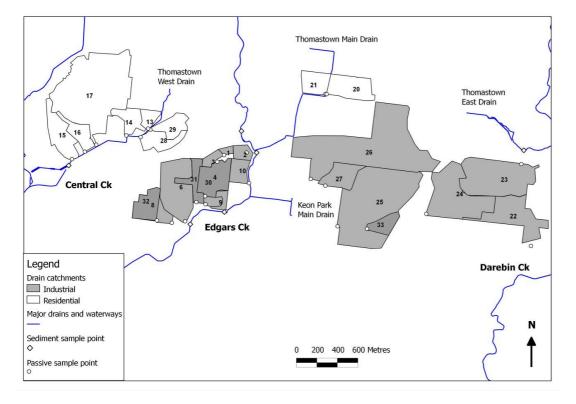


Figure 2. Sampling bags secured by cord (a), and by fastening plates using hook-and-loop fabric (b)



## Figure 3. Locations of drain catchments surveyed with passive samplers. Sub-catchments 4, 31, 32 and 33 were wholly contained within catchments 30, 30, 8 and 25 respectively.

After five weeks of sampling, mean pollutant concentrations were compared between catchments. In three catchments where consistently high pollution loads were identified, the catchment was divided into smaller sub-catchments in an attempt to locate the pollution source (Fig 3).

The third stage was a further five week survey of all catchments plus the additional sub-catchments identified in stage two.

### ANALYTICAL METHODS

Sediments were collected by filtration through a 63um nylon mesh sock. Both sediment and GAC media were stored at 4°C in 125mL glass jars until analysis. Pollutant concentrations in sediment and GAC media were determined by Australian Laboratory Services (ALS, 4 Westall Rd, Springvale, VIC, 3171) according to standard analytical methods. The heavy metals arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), silver (Ag) and zinc (Zn) were determined by ICP-AES after acid digestion (USEPA, 1983). Total mercury (Hg) was determined by FIMS. Volatile TPH fractions and benzene, toluene, ethylbenzene and xylene (BTEX), were determined by purge and trap capillary GC/MS after methanol extraction. Semi-volatile TPH fractions were determined by capillary GC/FID after DCM/acetone extraction, and quantified against alkane standards in the range C<sub>10</sub>-C<sub>36</sub>. Concentrations of volatile and semi-volatile petroleum hydrocarbon (PH) fractions were summed together with BTEX to yield a total petroleum hydrocarbon concentration (TPH sum). Moisture content was determined by mass loss after 12 hours drying at 103°C, and all concentrations reported as mg/kg dry weight. Quality control procedures included analysis of field and laboratory blanks, duplicate samples and determination of spike recoveries.

### DATA PROCESSING AND ANALYSIS

The major trends in pollutant concentrations were summarized by principal component analysis on the geometric mean concentrations of chromium, copper, nickel, TPH (sum) and zinc per catchment. Parametric analyses were restricted to those variables where at least 30% of values were above detection limits. Before the geometric mean was calculated, any values below detection limits were imputed using the regression on order method (Helsel, 2005).

The influence of catchment land use and rainfall was assessed by 2-way ANOVA for each of chromium, copper, nickel, TPH (sum) and zinc: pollutant concentration was the dependant variable, while land use and rainfall were factors. Comparisons across all catchments were made only after removing dependant sub-catchments (i.e.: catchments located downstream of another catchment in the same drain), and excluded field blanks.

Comparisons of pollutant loading between catchments were made by t-test of rank-transformed concentrations. Pollutant concentrations at each catchment were compared with those at site 1, since it was a small catchment with consistently low pollutant loadings and was sampled consistently throughout the program. The false discovery rate due to multiple sequential comparisons was controlled by adjusting p-values (Benjamini et al., 1995). Comparisons between catchments included dependant sub-catchments, since for locating pollution sources, we were primarily interested in differences between a catchment and its upstream sub-catchments. Although this dependence can be problematic for hypothesis testing, the effect is to increase the risk of failing to distinguish two catchments which in fact have different pollutant profiles. Therefore, where pairwise comparisons indicate a substantial difference between two catchments, this represents a conservative result.

### **Results and Discussion**

## SEDIMENT QUALITY TRANSECTS: SELECTED CONTAMINANT TRENDS FROM UPSTREAM TO DOWNSTREAM

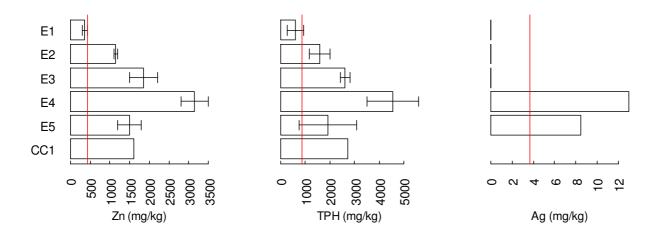


Figure 4. Sediment quality transects of heavy metals, hydrocarbons and silver along Edgar's Creek, and at the base of Central Creek, 2008-2010. Error bars represent standard errors (n=2). Sites locations are indicated on Figure 2, from upstream to downstream. For this survey, silver in sediment was measured in the 2008 pilot only (n=1). Reference line indicates sediment concentrations likely to cause adverse ecological effects for Zn and Ag (ANZECC/ARMCANZ, 2000), and probable effect concentrations for TPHs (Pettigrove et al., 2005).

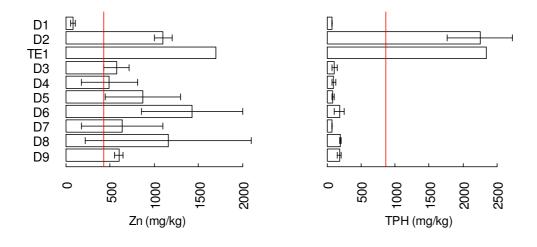


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### RAINFALL

During the study period, Melbourne received substantial rainfall compared with previous years (<u>http://www.bom.gov.au/climate/data</u>; accessed 24/05/2011). Approximately 250mm of rain fell from January 28<sup>th</sup> to May 12<sup>th</sup>, with at least 2mm of rain falling in nine of the ten sampling weeks. The majority of rain fell in two wet periods; about one third of the total was received in a single day on February 5<sup>th</sup>, while another third was received in the week ending April 14<sup>th</sup> (Fig 6). There was a five week break in sampling from the week ending March 4<sup>th</sup> to the week ending April 14<sup>th</sup> (Fig 6) to allow collation and preliminary analysis of results.

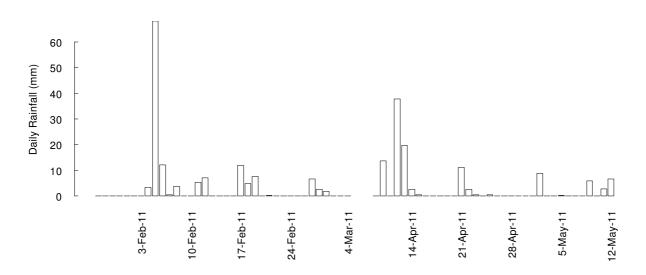


Figure 6. Daily (to 9AM) rainfall for the week prior to sample collection. Dates of sample collection given on x axis. Note the discontinuity in sampling dates from March 4<sup>th</sup> to April 14<sup>th</sup>. Rainfall was averaged across the study area by taking the mean of daily rainfall totals from the three weather stations illustrated in Fig 1.

### IMPACT OF RAINFALL AND CATCHMENT LAND USE ON POLLUTION LOADS

Catchment land use and rainfall both had substantial effects on pollutant accumulation, and the relative importance of each factor varied for different pollutants. Zinc and copper were strongly linked with industrial land use, while chromium and nickel were linked with increased rainfall. In general, hydrocarbons were influenced by an interaction between rainfall and land use, while the heavy metal pollutants were influenced by either catchment land use or rainfall (Table 1). Although these p values must be interpreted with caution due to the potential correlation of samples collected at the same site on different dates, some clear trends are apparent. The contrasting influence of rainfall on the relationship between land use and pollution was particularly striking in the case of zinc and TPHs (Fig 7).

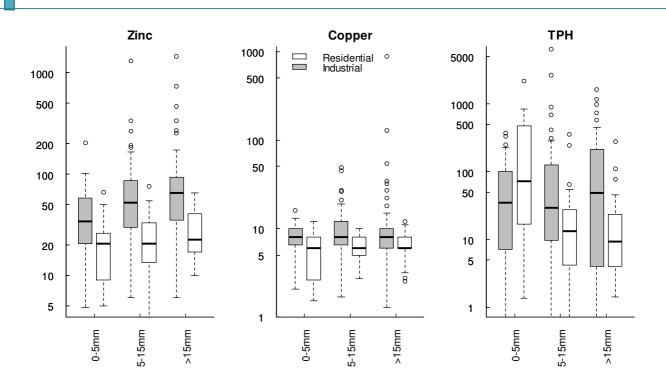
Table 1. Frequency of detection of common pollutants by GAC, and relative importance of catchment land use and rainfall as factors influencing pollutant accumulation (independent catchments only). Figures for Land use, Rainfall and land use x Rainfall are p values for a 2-factor ANOVA with pollutant concentration as dependant variable, and Rainfall and Land use as factors: p values >0.10 indicated by "ns". A space indicates no ANOVA was performed due to insufficient data. Method blanks were excluded from the analysis.

	1				x Rainfall
Arsenic 231	1	0.4%			
BTEX 231	17	7.4%			
Cadmium 231	2	0.9%			
Chromium 231	225	97.4%	0.003	0.001	ns
Copper 231	195	84.4%	< 0.001	ns	ns
Lead 231	12	5.2%			
Mercury 231	13	5.6%			
Nickel 231	229	99.1%	ns	0.012	ns
PH (sum of C <sub>6</sub> -C <sub>9</sub> ) 231	29	12.6%			
PH (sum of $C_{10}$ - $C_{36}$ ) 231	54	23.4%			
BTEX plus TPH (C <sub>6</sub> -C <sub>36</sub> ) 231	75	32.5%	0.016	ns	0.003
Silver* 39	5	12.8%			
Zinc 231	214	92.6%	< 0.001	0.002	ns

\*Silver was measured at only a subset of sites sampled across discontinuous date ranges, hence could not be included in the ANOVA.

Hydrocarbon concentrations were substantially more variable than zinc, with some catchments producing concentrations an order of magnitude greater than the median (Fig 7). Rainfall affected heavy metal and hydrocarbon pollution in quite different ways. Zinc accumulation was consistently higher in industrial than residential catchments, and was higher in wet than dry conditions irrespective of catchment land use. In contrast, TPH accumulation was dependent on both catchment land use and rainfall: in dry conditions, higher hydrocarbon concentrations tended to be found in residential catchments; in wet conditions, the reverse was true (Fig 7).

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# Figure 7. Effect of rainfall on the relationship between catchment land use and pollutant concentration in GAC (mg/kg). Zinc concentrations increased with rainfall, and were consistently lower in residential catchments. In contrast, increased rainfall was linked with more hydrocarbons from industrial catchments, but less from residential catchments.

The differing responses of heavy metals and hydrocarbons to rainfall reflect different pollutant sources and transport through the catchment. Atmospheric deposition and subsequent wash-off is an important source of heavy metals to stormwater (Davis et al., 2001), consistent with the observed increase in metal pollution with rainfall. The contrasting response of hydrocarbons to rainfall in catchments with different land use shows that in industrial catchments, heavy rainfall did not lead to cleaner stormwater runoff. Continuing high pollutant loads even after the "first-flush" of runoff (Lee et al., 2004), suggests hydrocarbon sources may be more concentrated in industrial areas. This would be consistent with the substantial reduction in hydrocarbon pollution previously observed after an industry stormwater education program in the City of Kingston (Marshall et al., 2008a).

### POLLUTANT TRENDS ACROSS CATCHMENTS

The major trends in pollutant loads between the independent catchments were summarized graphically by principle component analysis (Fig 8). The most obvious trend was for industrial catchments to have consistently higher and more variable pollution loads than residential ones, illustrated in Fig 8 by the clustering of residential catchments at left compared with the scatter of industrial catchments at right. By comparison, pollutant loads of residential catchments compared favorably with those of the field blanks (labeled "0" at left of figure 8).

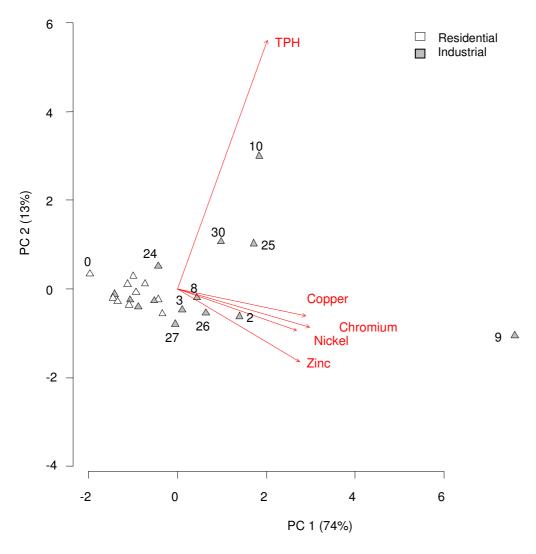


Figure 8. Principal component analysis of major pollutants accumulated by GAC (independant catchments only). Not all catchments are numbered for clarity. Field blanks included for comparison, labeled catchment 0 at left.

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### COMPARISON OF POLLUTION LOADS BETWEEN CATCHMENTS

For most pollutants, loads varied substantially between catchments. The only pollutants measured which did not vary between catchments were mercury and BTEX. Catchment 1 was used as a benchmark to compare all other catchments, since it consistently returned low-to-moderate pollutant loads and hence serves as a conservative estimate of background pollutant loads in both residential and industrial areas. Note that catchment maps are coloured by the geometric mean concentration of pollutant accumulated by GAC. Boxplots illustrate the median concentration, and indicate (\*) which catchments differed significantly from catchment 1 based on pair-wise t-tests of ranked concentrations. The only exception to this was silver, which was compared with catchment 4 since silver was not determined in GAC from catchment 1

### ARSENIC

Arsenic was detected only in catchment 33, and on only one occasion. Although this constitutes a substantially higher detection rate than background, this should be interpreted cautiously, since it was dominated by a single event where 12mg/kg was measured (Fig 9).

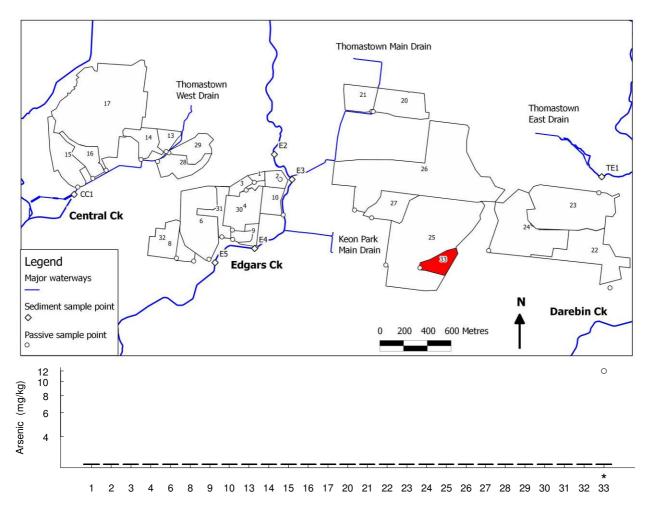


Figure 9. Spatial distribution of arsenic concentrations and variation between catchments. Catchments which differ significantly from 1 (p<0.05) indicated by \*

### CADMIUM

Cadmium was detected from only two catchments, and only at sub-catchment 33 were concentrations high enough to raise concerns (Fig 10). This result again must be interpreted carefully due to the low frequency with which measurable concentrations of cadmium were detected in GAC media.

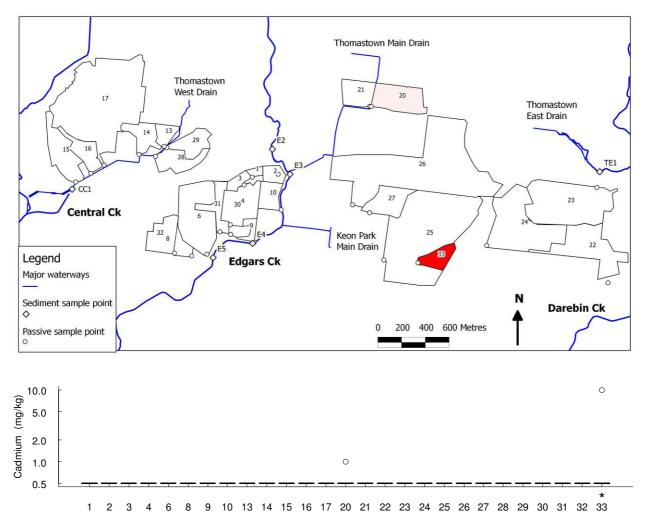


Figure 10. Spatial distribution of cadmium concentrations and variation between catchments. Catchments which differ significantly from 1 (p<0.05) indicated by \*

### CHROMIUM

Chromium was detected in almost every sampling event. This is at least partly due to the basalt geology in the Thomastown region, where background concentrations are higher than other regions of Melbourne (Pettigrove et al., 2003a). In spite of these background concentrations, catchment 9 consistently produced significantly high chromium concentrations, indicating a possible point source (Fig 11).

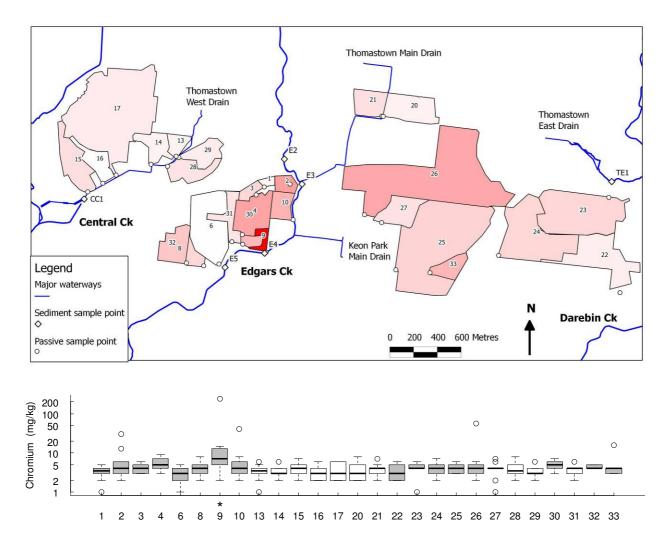


Figure 11. Spatial distribution of chromium concentrations and variation between catchments. Catchments which differ significantly from 1 (p<0.05) indicated by \*

### COPPER

Copper loads were consistently elevated in catchment 25, and even higher in sub-catchment 33 (Fig 12). A similar pattern was noted in sub-catchment 32 with respect to catchment 8. This suggests a substantial proportion of the copper load from catchments 25 and 8 could be attributed to sub-catchment 33 and 32 respectively. Catchments 2, 3 and 9 also had substantially higher copper loads, with a maximum copper concentration of 876mg/kg recorded at catchment 9. In spite of this high peak load at catchment 9, sub-catchment 33 had the highest mean (64.8 vs 29.1mg/kg) and median (50 vs 18mg/kg) copper concentrations.

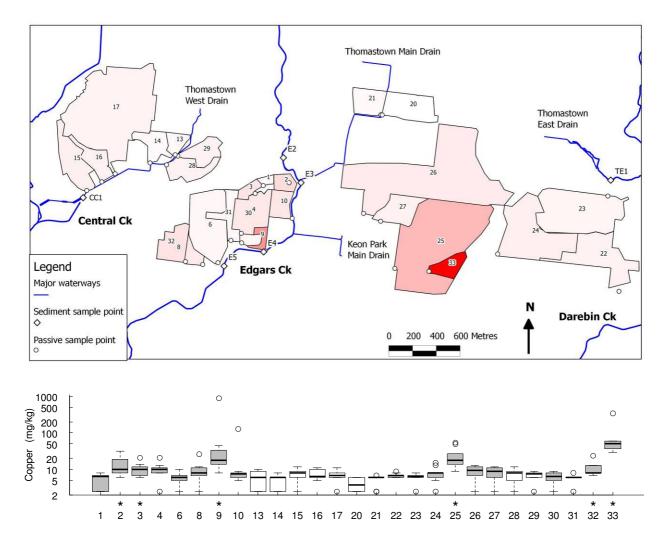


Figure 12. Spatial distribution of copper concentrations and variation between catchments. Catchments which differ significantly from 1 (p<0.05) indicated by \*

### Lead

Lead concentrations in GAC media were rarely above the limit of detection (Fig 13). Although lead was detected twice at catchments 2, 4 and 9, with a peak of 54mg/kg, it was consistently elevated only at sub-catchment 33. The highest concentration recorded was 195mg/kg from catchment 26. This sample was visibly contaminated with a yellow-brown metallic residue (Fig 14), and was associated with high concentrations of zinc as well as lead.

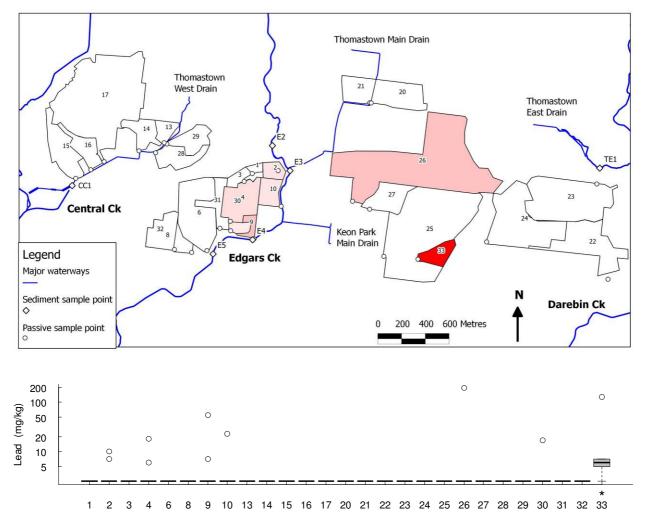


Figure 13. Spatial distribution of lead concentrations and variation between catchments. Catchments which differ significantly from 1 (p<0.05) indicated by \*



Figure 14. Metallic residue on passive sampler retrieved 6<sup>th</sup> May from catchment 26.

### MERCURY

Mercury was rarely detected at any catchment. The highest concentration measured was 2.9mg/kg, at sub-catchment 33 on April 15<sup>th</sup> (Fig 15). The only catchment where it was detected more than once was catchment 1. This is unlikely to represent a significant source of mercury to Edgar's Creek, since one of these samples was at the limit of detection (0.1mg/kg) and the other marginally higher (0.2mg/kg).

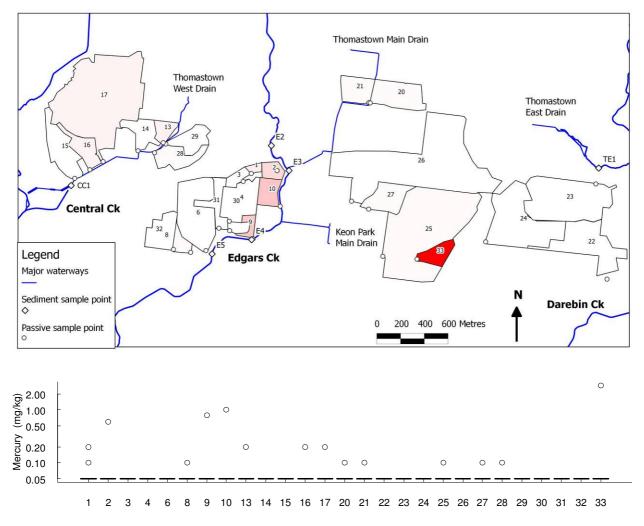


Figure 15. Spatial distribution of mercury concentrations and variation between catchments. Catchments which differ significantly from 1 (p<0.05) indicated by \*

### Nickel

Nickel concentrations were mostly in the range 5-10mg/kg. This probably represents the background concentration associated with urban catchment on basalt soils (Pettigrove et al., 2003a), and the only instance where nickel was below detection limits was at catchment 23 on May 13<sup>th</sup>. Only catchment 9 was consistently elevated, with a mean concentration of 12.7mg/kg, and the highest peak concentration of 144mg/kg (Fig 16).

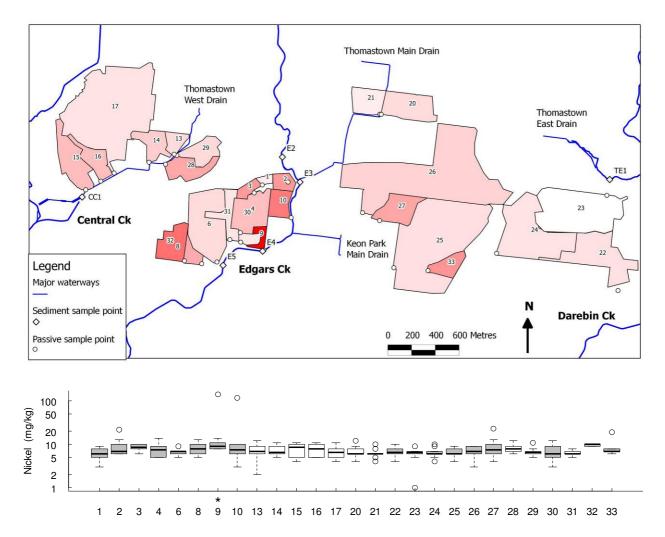


Figure 16. Spatial distribution of nickel concentrations and variation between catchments. Catchments which differ significantly from 1 (p<0.05) indicated by \*

### Silver

Silver is rarely found in urban sediments, but is potentially a highly toxic pollutant (ANZECC/ARMCANZ, 2000). It was hence surprising to find such persistently high concentrations in Edgar's Creek sediment downstream of Keon Park Main Drain (sediment collection points E4 and E5 on Fig 1). Inside this drain, silver was detected only from catchment 25 and sub-catchment 33 (Fig 17). The consistent presence of silver from catchment 25 indicated a probable point source in this area. Further sampling localized this source to sub-catchment 33. The regular presence of silver from sub-catchment 33, together with the high peak loads observed (157mg/kg on April 15<sup>th</sup>), make it a credible source of the elevated silver concentrations in Edgar's Creek and downstream.

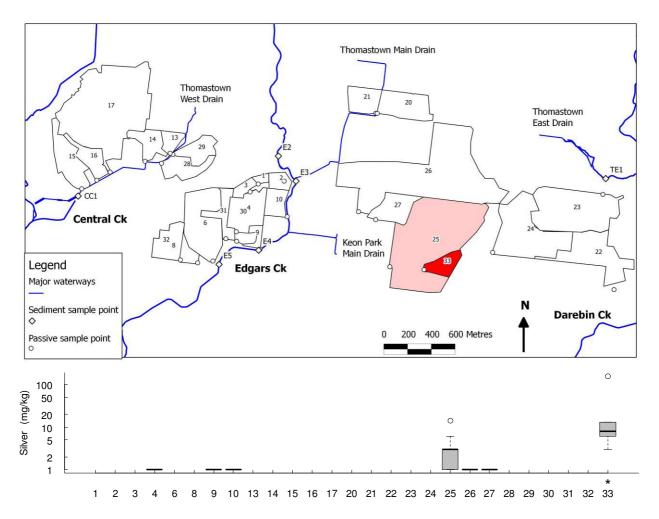


Figure 17. Spatial distribution of silver concentrations and variation between catchments. Catchments which differ significantly from 4 (p<0.05) indicated by \*

### ZINC

More than any other pollutant measured, zinc concentrations varied with catchment land-use (Fig 18, Table 1). Of the 14 catchments with consistently elevated zinc loads, 13 were classified as predominately industrial land use (Fig 18). Although catchment 30 had mean zinc loadings of 111mg/kg, much of this could be attributed to sub-catchment 4, which had a mean zinc loading of 235mg/kg. The same pattern was observed in sub-catchment 33 (mean loading 165mg/kg) with respect to catchment 25 (80mg/kg). In contrast, the moderately high mean loading in catchment 8 (72mg/kg) could not be attributed to sub-catchment 32 (54mg/kg). The highest concentration recorded was 1450mg/kg at catchment 9, although a peak of over 1300mg/kg was recorded at both catchments 26 and 33 on separate occasions. The maximum of 1310mg/kg at catchment 26 coincided with high concentrations of lead and visible fouling observed on May 6<sup>th</sup> (Fig 14).

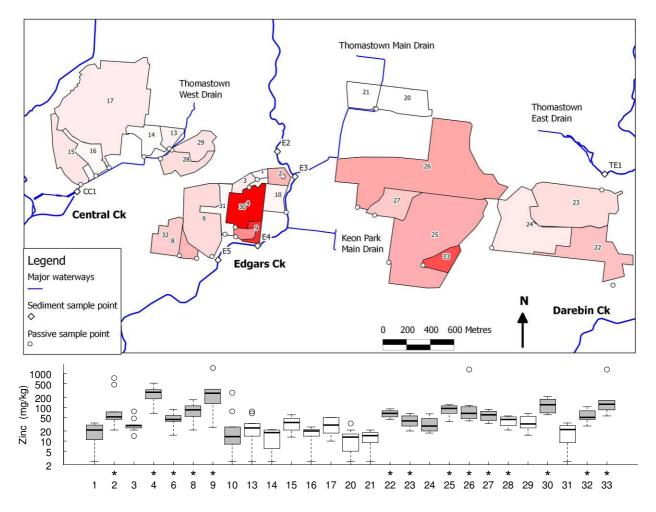


Figure 18. Spatial distribution of zinc concentrations and variation between catchments. Catchments which differ significantly from 1 (p<0.05) indicated by \*

### BENZENE, ETHYLBENZENE, TOLUENE AND XYLENE (BTEX)

Volatile aromatics (BTEX) were detected sporadically at most catchments, but no single catchment stood out as heavily polluting (Fig 19). Although catchment 23 had the highest geometric mean loading (1.6mg/kg), this measure was strongly influenced by a single sample collected on Feb 10<sup>th</sup>, which contained 22.9mg/kg BTEX.

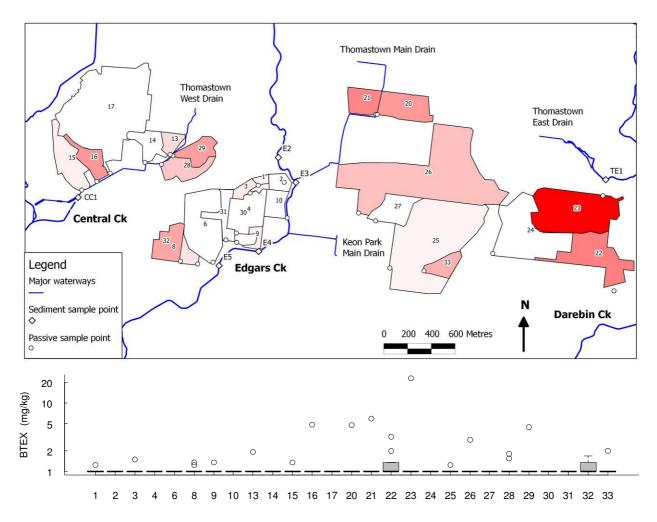


Figure 19. Spatial distribution of BTEX concentrations and variation between catchments. Catchments which differ significantly from 1 (p<0.05) indicated by \*

### TOTAL PETROLEUM HYDROCARBONS (TPH)

Petroleum hydrocarbons (TPHs) were common in catchments with industrial landuse. All the 8 catchments where the median loading exceeded combined detection limits, and both catchments with consistently elevated TPHs, were classed industrial. A substantial proportion of the TPH load of catchment 30 (mean 150mg/kg) could reasonably be attributed to sub-catchment 4 (mean 281mg/kg), which also recorded the highest peak load (19,705mg/kg). By comparison, in catchment 10 the peak load was a relatively modest 995mg/kg, but TPHs were present in 7 out of 10 samples. An oily residue covered the passive sampler collected from catchment 13 on May 6<sup>th</sup> (Fig 21), but this was associated with only a modest spike in TPHs.

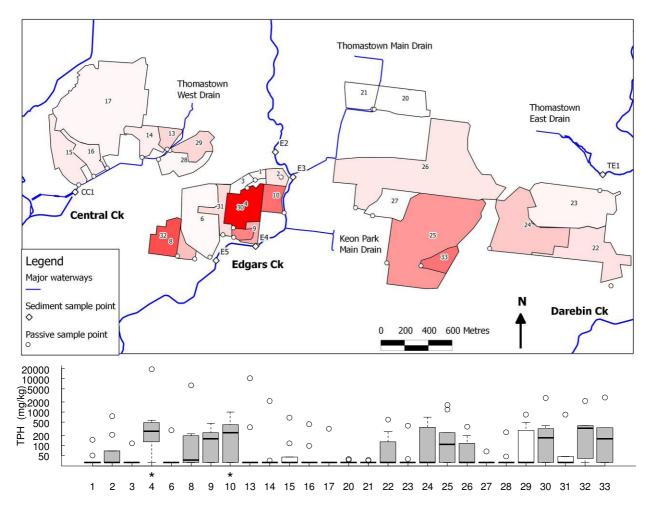


Figure 20. Spatial distribution of TPH concentrations and variation between catchments. Catchments which differ significantly from 1 (p<0.05) indicated by \*



Figure 21. Oily residue on passive sampler retrieved 6<sup>th</sup> May from catchment 13.

### Conclusions

The pilot study conducted in 2008 confirmed the feasibility of passive sampling technology for pollution surveys at sub-catchment scale. This initial sediment quality survey found Edgar's Creek sediment contained heavy metals and hydrocarbons substantially above environmental guidelines, and identified potential pollution hotspots between Mahoney's Rd and the Thomastown Main Drain. Steep increases in pollution were apparent below drain outfalls such as Keon Park Main Drain (Figs 4 and 5), suggesting disproportionate pollution loads coming from relatively small catchments. Finally, the passive sampling survey identified consistent contamination patterns, specific to polluting sub-catchments (Figs 9 to 20). These sub-catchments were identified as 'hot spots' for stormwater pollution, with the specific contamination pattern a useful indicator of the likely source.

Contaminant loads were consistently high in four industrial sub-catchments. Sub-catchment 33 was of particular interest due to elevated silver loads, as well as a broad range of heavy metals including arsenic, cadmium, copper, lead, mercury and zinc. This small sub-catchment is dominated by a silver-recycling facility, which is probably the source of the persistent silver contamination in Edgar's Creek and Leamington St wetlands downstream. Catchment 9 had consistently high chromium, copper, nickel and zinc loads, although no obvious metal-plating, engineering, or automotive recycling activities were apparent in this catchment. Catchments 4 and 10 consistently produced high hydrocarbon loads; although again, no obvious sources were apparent. To definitively identify the pollution sources in these sub-catchments, inspection of individual premises will be required.

Industrial land use in the survey area was unequivocally associated with elevated stormwater pollutant loads. In general, sub-catchments with the highest pollutant loads were located immediately upstream of sediment pollution hotspots identified in the stream sediment survey. This suggests a substantial proportion of pollution entering this section of Edgar's Creek could come from a small minority of industrial sub-catchments.

### Recommendations

The passive sampling survey showed industrial land use was clearly associated with elevated stormwater pollutant loads, and identified individual sub-catchments with characteristic pollutant profiles. Catchments with consistently high pollutant loadings should be a high priority for future stormwater education programs. A coordinated strategy to reduce pollution entering Edgar's, Darebin, and Central Creeks via stormwater should include the following:

- 1. Investigation by EPA Victoria of all premises in polluting catchments: 33, 9, 10 and 4.
- 2. A stormwater education and enforcement program for industrial areas, particularly in areas not covered by previous programs (BMT WBM Pty Ltd, 2009).
- 3. Follow-up monitoring to assess the effectiveness of actions 1 and 2.

In the case of catchments 33, 9, 10 and 4, the ongoing pollution issues have been referred to EPA Victoria for investigation, currently in progress. To assess the reduction in pollution as a result of both this investigation, and future stormwater education programs, follow-up monitoring of pollution loads in both drains and receiving waterways is strongly recommended.

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