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Metal levels in street sediment from an industrial city: spatial trends, chemical fractionation, and management implications

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Abstract

Background, aim and scope Street sediment samples were collected at 50 locations in a mixed land use area of Hamilton, Ontario, Canada, and metal levels were analyzed using a sequential extraction procedure for different particle size classes to provide an estimate of potential toxicity as well as the potential for treatment through best management practices (BMPs).

Methodology The street sediment samples were dry sieved into four different particle size categories and a sequential extraction procedure was done on each size category following the methodology proposed by Tessier et al. 1979 using a Hitachi 180-80 Polarized Zeeman Atomic Absorption Spectrophotometer.

Results and discussion Analysis of variance, post hoc leastsignificant difference tests, and kriging analysis showed that spatially Mn and Fe levels were associated with a well-defined heavy industrial area that includes large iron- and steelmaking operations; Cu and Pb were associated with both the

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industrial and high-volume traffic areas, while Zn tended to be more associated with high-volume traffic areas. The potential bioavailability of the metals, based on the sum of chemical fractions 1 (exchangeable) and 2 (carbonate-bound), decreased in order: Zn > Cd > Mn > Pb > Cu > Fe. Based on aquatic sediment quality guidelines, there is some concern regarding the potential impact of the street sediment when runoff reaches receiving waters.

Conclusions It is possible that a combination of BMPs, including street sweeping and constructed wetlands, could help to reduce street sediment impact on environmental quality in the Hamilton region. The data presented here would be important in developing and optimizing the design of these BMPs.

Keywords BMPs \cdot Kriging \cdot Metals \cdot Sequential extraction \cdot Street sediment \cdot Street sweeping \cdot Urban runoff

1 Background, aim, and scope

Street sediment within urban areas represent a repository of multiple contributing sources of pollution including automobile emissions, urban infrastructure degradation and erosion, and other particulate nonpoint sources from short- and longrange atmospheric deposition (Vermette et al. 1987, 1991; Sutherland 2003). Street sediment is a significant source of metals with possible human health risks resulting from prolonged exposure and inhalation (Miguel et al. 1999) and can negatively impact receiving water body quality during runoff events (Zarriello et al. 2002; Droppo et al. 2006). Within the study area, there is extensive research available on contaminated bed sediments of Hamilton Harbor (Krantzberg and Boyd 1992; Krantzberg 1994; Zeman and Patterson 2003); however, there is limited work relating street sediment

contamination as a possible source of pollution to the harbor (Irvine et al. 1998; Droppo et al. 2002).

Much of the street sediment research to date has been directed at the characterization of the elemental composition to better ascertain pollutant sources and/or the degree to which they may contribute to the degradation of aquatic resources (e.g., Field et al. 2000; Sutherland 2003; Irvine et al. 2005; Robertson and Taylor 2007; Sutherland et al. 2007). Higher metal levels generally tend to be associated with the finer (<63 um) street sediment sizes (Stone and Marsalek 1996; Sutherland 2003; Herngren et al. 2006). These fine sediments are more likely to be hydraulically sorted from street deposits (often coarse grained in nature) and transported to and within storm and/or combined sewer systems during rain events with subsequent delivery to receiving water bodies or sewage treatment plants (Droppo et al. 2002). Often, however, street sediment samples are analyzed in bulk and do not account for the contributions of different size fractions or the impact of hydraulic sorting (Stone and Marsalek 1996; Droppo et al. 2002; Sutherland and Tack 2007). Sample analysis that does not account for the differential metal contributions of grain sizes has been shown to underestimate the relevant concentration entering an urban water body or sewer system (Sutherland 2003; Droppo et al. 2006). In addition, while sequential extraction (Tessier et al. 1979), or variations thereof (e.g. Sutherland and Tack 2007), has been used to investigate the partitioning of metals within various compositional fractions of sediments, and for the inference of bioavailability (Gibson and Farmer 1984; Hamilton et al. 1984; Ramlan and Badri 1989; Stone and Marsalek 1996; Sutherland 2002, 2003; Lee et al. 2005; Manno et al. 2006), bulk metal analysis is still the norm in policy-driven research (Pitt et al. 2004, 2005).

Many urban pollution control programs such as the US Environmental Protection Agency's (EPA) Combined Sewer Overflow Control Policy (40 CFR Part 122) and the Great Lakes 2000 Cleanup Fund of the Municipal Wastewater Program were developed to facilitate and encourage the mitigation and remediation of pollution from municipal sources through the use of best management practices (BMPs) such as street cleaning and retention/detention basins (US EPA 1995a, b; Kok et al. 2000). The design of surface runoff mitigating BMPs requires information on street sediment characteristics (e.g., metal partitioning by grain size) for their effective implementation and operation. Towards this end, 50 bulk street sediment samples were collected from a sewershed area in Hamilton, Ontario, Canada and fractionated into four size classes ranging from <63 to 2,000–500 µm. These size fractions were then analyzed for Cd, Cu, Fe, Mn, Pb, and Zn using a sequential extraction technique to provide partitioning information (exchangeable, bound to carbonates, bound to Fe/Mn oxides, bound to organic matter, residual). This

generated a data set of 1,000 metal concentrations which was used to assess spatial trends (using global information system) of total metal concentrations (normalized by size fraction contributions) and grain-size-specific metal concentrations and to determine potential bioavailability within the street sediments. Potential bioavailable levels were compared to regulatory sediment guidelines to provide an estimate of potential toxicity as well as the potential for treatment and management. An illustrative example of the possible load reduction in bioavailable metals due to street sweeping is provided together with a discussion of BMP implementation options using existing infrastructure.

2 Materials and methods

2.1 Location of the study area

The Kenilworth sewershed (Fig. 1) has a contributing area of 256.6 ha and discharges to the Woodward Sewage Treatment Plant or to Hamilton Harbor, Lake Ontario, via a single combined sewer overflow (CSO) during rainfall events of greater than 5 mm (Paul Theil Associates and Beak Consultants 1991). The sewershed is relatively flat (1% slope on average), with the exception of the Niagara Escarpment, and can be divided into two sections. The upper portion of the sewershed contains approximately 52% impervious land and is dominated by older, residential, single-family dwellings, with commercial ribbons along major streets. The lower portion of the sewershed (approximately 9% of the contributing area) has mixed industrial practices with steel manufacturing being dominant. Sixty-six percent of the industrial area can be considered impervious with extensive unpaved industrial storage lots. It is estimated that the total combined sewage overflow volume from the sewershed for a typical rainfall year is 311,000 m³ (Irvine et al. 1998).

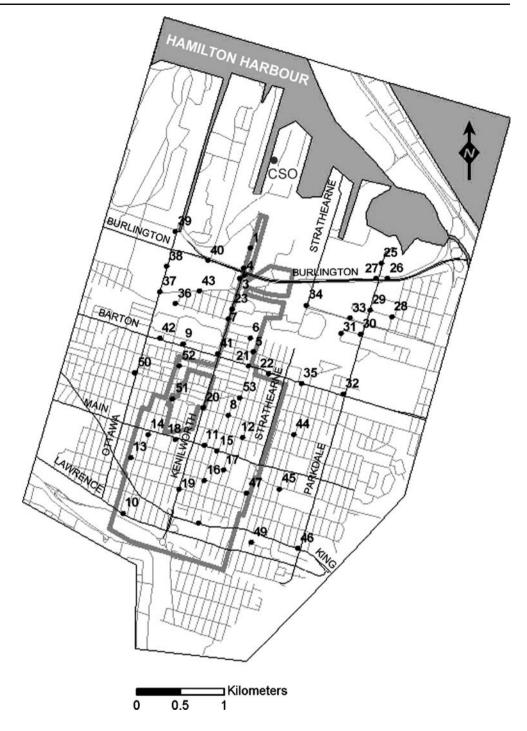
Dry surface street sediment samples were collected from the gutters at 50 sites located throughout the sewershed and external to its boundaries (see Fig. 1) on 14 May 2001. Fifteen sites represented industrial land use, as these sites had at least one side of the street adjacent to an industry or an industrial storage lot regardless of traffic volume. Seventeen sites were classified as high-traffic-volume commercial/residential sites (between 13,560 and 70,137 vehicles per 24-h period). Eighteen sites were defined as low-traffic-volume (<13,560 vehicles per 24-h period) commercial/residential sites.

2.2 Sample collection and particle sizing

Each bulk dry street sediment sample was gathered with a polyethylene scoop and placed in a 500-ml polyethylene



Fig. 1 Sampling sites in and around the Kenilworth sewershed of Hamilton, Ontario, Canada. *Heavy gray line* delineates the Kenilworth sewershed contribution area. Note that sites 2, 24, and 48 did not yield enough sample mass for size fractionation and so are not included in the data set or figure



container. The scoop was washed with acetone and distilled water prior to each sample collection. Samples were airdried and split into two samples using a rotating V-splitter run for 2 min. One sample was analyzed for bulk fractionated metal concentrations while the other was further fractionated into four size classes (2,000–500, 500–250, 250–63, <63 µm) using standard sieving methods prior to metal fractionation analysis. To minimize contamination issues, the sieves used in the size fractionation were stainless steel and they were rinsed with acetone and

distilled water between each sample analysis. Results for the bulk of chemically fractionated metals are discussed by Droppo et al. (2006) while this paper focuses on the results for the chemical fractionation within the different sediment size classes.

2.3 Metal analysis

All 50 grab samples of street sediment were analyzed using the sequential extraction procedure of Tessier et al. (1979)



with a Hitachi 180-80 Polarized Zeeman Atomic Absorption Spectrophotometer at the National Water Research Institute (NWRI). This method separates the metals into the following operationally defined fractions; fraction 1: exchangeable; fraction 2: bound to carbonates; fraction 3: bound to Fe/Mn oxides; fraction 4: bound to organic matter; fraction 5: residual. While metal fractionation data alone cannot be used to directly address bioavailability, the sequence of extraction (fraction 1 to fraction 4) can be viewed as an inverse scale of the relative availability of metals (fraction 5 is considered not available; Stone and Droppo 1996). Following the methods of Lee et al. (2005), this paper uses the sum of fractions 1 and 2 to represent the "bioavailable" fraction. While no standard exists for sequentially extracted metals, the sediment metal standard WQB-1 (NWRI 1990) was analyzed with respect to total metals with each run of samples providing a measure of QA/QC. All standard runs resulted in total metals concentrations within the certified range of concentrations.

2.4 Data analysis

To examine whether the different land uses had a significant relationship with the spatial distribution of metal levels in the street sediment, the BestFitTM option within the Risk Analysis and Simulation software (@Risk version 4.5, an Excel spreadsheet add-in, Palisade Corporation 2005) was used to determine which probability distribution function best fit the data. BestFitTM compared the sample data with 21 theoretical probability distributions, using a maximum likelihood estimator approach. Subsequently, chi-squared, Kolmogorov-Smirnov, and Anderson-Darling test statistics were calculated to evaluate goodness of fit and BestFitTM ranked the fit of each distribution based on the test statistic results. The rankings of the most appropriate distributions may differ for the test statistics because of different emphasis in the calculation of the statistics (Palisade Corporation 2005). An examination of the top three rankings for each metal and each statistic indicated that the log-logistic and lognormal distributions were most appropriate for the data. Because the log-logistic and lognormal distributions were most appropriate, a base-10 logarithm (log₁₀) transformation was applied to the raw data for subsequent statistical and geospatial analyses.

One-way analysis of variance (ANOVA) and post hoc least-significant difference (LSD) t tests were used to investigate the relationship between land use and the mean total and chemically fractioned metals levels with SPSS 16 statistical software (α =0.05 for all tests). The mean total concentration in this case was calculated using each of the five chemical fractions normalized by the proportion of sediment size. The "size normalization" for total concentration of a sample was calculated as the sum of each

chemical fraction concentration weighted by the proportion of the total street sediment mass in each sediment size class. If the relationship was significant, a kriging approach was used to predict the spatial distribution of metal levels in street sediment. Kriging is appropriate when data are spatially autocorrelated or have a directional bias and often is used in soil science. The Geostatistical Analyst tool in ArcGIS 9.2 was used to perform ordinary kriging analysis. Default parameters were used on a log₁₀ transformation of the data. Ordinary kriging assumes a constant unknown mean and assumes that points spatially closer to each other are more similar than those that are further apart. The spherical semivariogram model was used. This model is most often used when the data show a decrease in spatial autocorrelation with distance. The search neighborhood was set to a maximum of five neighbors and a minimum of two.

3 Results and discussion

3.1 Spatial distribution of metals

Mean total metal levels by land use and the levels by chemical fraction are shown in Table 1. With the exception of Cd, mean total metal levels of street sediment were significantly related to land use (p=0.05). One-way ANOVA and LSD results demonstrated that the highest metal levels were observed at the industrial sites for Fe and Mn; commercial/residential with high traffic volume sites had high Zn, and both industrial and commercial/residential with high traffic volume had high Cu and Pb $(\alpha=0.05)$. All maps produced by the kriging for each total metal supported the ANOVA and LSD analysis. Copper, Fe, Mn, and Pb were strongly loaded in industrial areas (and to some extent the high-volume traffic areas; Fig. 2a–c, f) while Zn was mainly distributed in the commercial/residential with high traffic volume areas (see Fig. 2d).

Vermette et al. (1987) previously showed that Mn was a signature element for the iron- and steel-making industry in Hamilton and this earlier work reported a similar spatial trend for Mn levels in street sediment as observed in this study. Legorburu and Millan (1986) also reported that a steel mill in Spain was a significant source of Fe, Zn, and Mn in air, grass, and soil samples and levels declined with distance from the steel mill. Although Li et al. (2006) found that Mn levels in urban lake sediments were increasing as the result of methylcyclopentadienyl manganese tricarbonyl being used in place of tetraethyl lead as a fuel additive, the dominant source of Mn in Hamilton appears to be the steel mills. Levels of Fe, Zn, Pb, Al, Cu, Cr, and Mn were reported as being highest in an industrial area of Australia, as compared to residential and commercial areas, although vehicle traffic also was greater in the industrial area and the



Table 1 Mean total concentrations and mean concentrations by chemical fraction (µg/g) for different land uses

Land use	Mean total	Mean total concentration, μg/g, this study ^b	Mean chemical fraction, μg/g ^c				
	concentration, μg/g (from Droppo et al. 2006) ^a		Fr1	Fr2	Fr3	Fr4	Fr5
Cd-Ind	6.1	2.2 ^d	0.06	0.45	0.56	0.49	0.59
Cd-C/R-H	4.7	$2.0^{\rm d}$	0.08	0.33	0.54	0.34	0.72
Cd-C/R-L	1.9	1.5 ^d	0.12	0.29	0.28	0.19	0.58
Cu-Ind	162	171 ^d	0.87	5.1	8.7	53.4	103
Cu-C/R-H	119	164 ^d	1.6	12.6	11.7	50.9	87.7
Cu-C/R-L	61	73.5 ^d	1.3	6.9	5.1	21.4	39.1
Fe-Ind	54,444	99,829 ^d	2.7	308	13,484	1,449	87,360
Fe-C/R-H	43,150	61,207 ^d	4.5	251	5,447	806	54,699
Fe-C/R-L	23,483	28,207 ^d	4.4	141	2,529	800	24,762
Mn-Ind	4,642	6,658 ^d	2.3	791	2,177	734	3,036
Mn-C/R-H	2,375	3,032 ^d	3.8	456	949	273	1,351
Mn-C/R-L	1,344	1,514 ^d	4.8	325	516	149	628
Pb-Ind	219	276 ^d	1.2	18.1	86.1	32.3	121
Pb-C/R-H	132	165 ^d	0.88	6.7	65.5	24.5	56.8
Pb-C/R-L	73	84.9 ^d	0.78	3.5	29.9	9.3	36.0
Zn-Ind	428	390^{d}	1.2	120	92.0	64.4	118
Zn-C/R-H	583	544 ^d	3.3	153	104	53.5	162
Zn-C/R-L	544	413 ^d	3.5	99.3	86.6	50.0	135

Chemical fraction 1 (Fr1) is exchangeable; chemical fraction 2 (Fr2) is bound to carbonates; chemical fraction 3 (Fr3) is bound to Fe/Mn oxides; chemical fraction 4 (Fr4) is bound to organic matter; chemical fraction 5 (Fr5) is residual

Ind industrial, C/R-H commercial/residential with high traffic volumes, C/R-L commercial/residential with low traffic volumes

higher levels of Zn, Fe, and Pb may have been related to the traffic (Herngren et al. 2006). Levels of Pb, Cu, Zn, Fe, and Mn were significantly related to traffic density in a study conducted in Hong Kong (Ho and Tai 1988). Zinc levels can be surprisingly high in used motor oil and Zn also is found in transmission fluid, tire wear particles, and asphalt (Harrison 1979; Breault et al. 2005) and this may explain the spatial trend for Zn in our study. Interestingly, the kriging results showing high Pb levels in the industrial area may have been extended further south because the highest Pb level (2,302 μ g/g) was found at site 3, towards the southern edge of the industrial area. A Pb recycling facility was located next to this site at the time of sampling.

3.2 Potential bioavailability

To assess the potential risks associated with the metals levels in the study area, the chemical fractions were

examined. Table 1 summarizes the chemical fraction by land use for each metal and Fig. 3 shows the distribution of the chemical fractions by street sediment particle size class (with all land uses together).

Of all the metals, Cd exhibited the highest percentage of chemical fraction 1 while Cu, Fe, and Mn had the highest percentage in fraction 5 (see Fig. 3). Cadmium is considered more mobile than other metals, with binding generally through cation exchange and easily reducible phases (Solomons and Förstner 1984). High bioavailability of Cd in stormwater runoff also has been found by others (e.g., Hamilton et al. 1984; Ellis et al. 1987).

The spatial distribution of total Mn (sum of fractions 1 through 5 in the <63-μm size class) in Fig. 4f reflects influences from fractions 2, 3, 4, and 5, which are visually similar (see also Fig. 3). In contrast, the spatial distribution of each chemical fraction (in the <63-μm size class) for Zn (Fig. 5) differs and the total Zn spatial distribution (see Fig. 5f) reflects influence from all fractions.



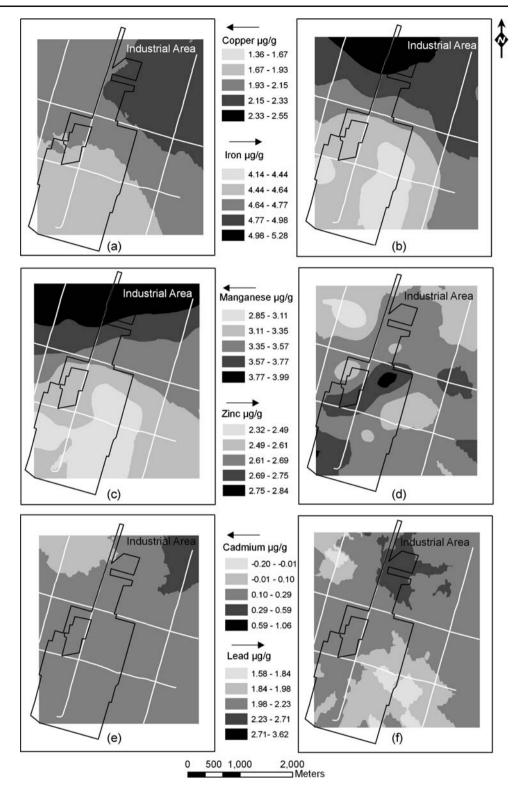
^a Sum of chemical fractions 1 through 5 for bulk (i.e., not size fractionated) samples

^b Sum of fractions 1 through 5 normalized by sediment particle size

^c Concentration normalized by sediment particle size

^d Summarized results of the LSD tests for difference in metals concentrations between land use (α =0.05). For example, the mean concentration in Cu was significantly less for the C/R-L land use than in the Ind and C/R-H land uses

Fig. 2 a–f Kriging analysis of total concentration for each metal (log10 of microgram per gram) within street sediment in the Kenilworth sewershed of Hamilton, Ontario, Canada. The white lines represent major roadways and the outline of the Kenilworth sewershed also is overlaid



The distribution of chemical fractions between different particle size classes for a particular metal is similar. However, the distribution of chemical fractions between the different metals can be quite different (see Fig. 3). For example, the distribution of chemical fractions in the different particle size classes shows a relatively similar pattern for Fe (with a high

proportion in fraction 5 for all sizes). The chemical fraction distribution across all sizes for Fe is quite different from the chemical fraction distribution across all sizes for Cd (see Fig. 3). As such, it does not appear that there is a particular advantage to optimizing BMPs to remove a particular size class with the expectation of removing a specific chemical



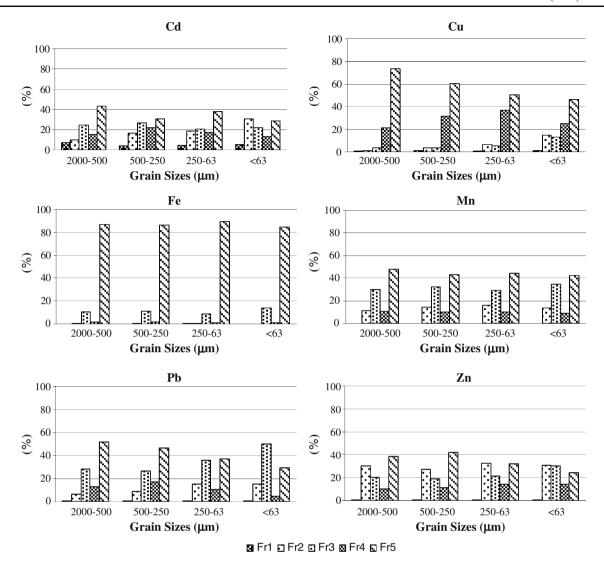


Fig. 3 Percentage of chemical fraction distributed by size classes in Cd, Cu, Fe, Mn, Pb, and Zn. Chemical fraction 1 (*Fr1*) is exchangeable; chemical fraction 2 (*Fr2*) is bound to carbonates;

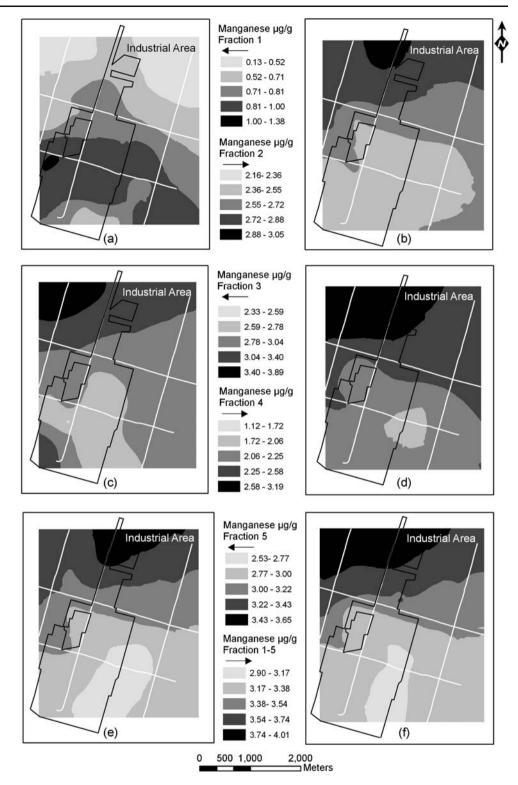
chemical fraction 3 (Fr3) is bound to Fe/Mn oxides; chemical fraction 4 (Fr4) is bound to organic matter; chemical fraction 5 (Fr5) is residual

fraction. Fractions 1 and 2 levels were highest in the <63-µm sediment size class for Cd and Cu, but for Fe, Mn, Zn, and Pb levels they also could be highest in the 250–63-μm range. This suggests that if a combination of BMPs targets the two smaller size classes (up to 250 µm), a reasonable proportion of the bioavailable metal fractions could be addressed. Conservatively, using fractions 1 and 2 (e.g., the exchangeable and carbonate-bound fractions) as the most readily available (rather than fractions 1 through 4), the comparative bioavailability of metals (normalized by size fraction) decreased in the order of Zn > Cd > Mn > Pb > Cu > Fe. Lee et al. (2005) found that the comparative ranking of metals decreased in the order of Zn > Ni > Cd > Pb > Cu > Cr for their study of street sediment in Seoul, South Korea. Although not all of the metals are common, the relative order of the common metals is similar between the two studies.

In considering fractions 1 and 2 as the most bioavailable, the sum of these fractions is compared to the Ontario Ministry of Environment and Energy (MOEE 1993) guideline for aquatic sediment (Table 2). As noted above, many studies do not chemically fractionate street sediment samples and the mean total concentrations (all land uses together) also are shown in Table 2 for comparison. The MOEE defines the lowest effect level (LEL) as a level of contamination that can be tolerated by the majority of sediment-dwelling organisms and levels above the LEL are considered marginally polluted. Furthermore, the severe effect level (SEL) indicates a level of contamination that is expected to be detrimental to the majority of sediment-dwelling organisms and levels above the SEL are considered heavily contaminated. The mean level of Zn and Mn (fraction 1 and 2) was greater than the LEL while no mean levels (fraction 1 and 2) were greater



Fig. 4 a–f Kriging analysis showing the spatial distribution of Mn (log10 of microgram per gram) in each chemical fraction (sediment size class <63 μm). The *white lines* represent major roadways and the outline of the Kenilworth sewershed also is overlaid

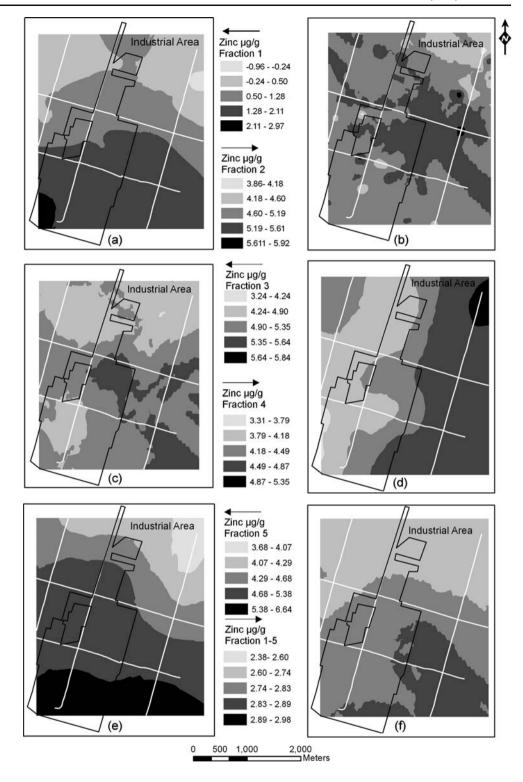


than the SEL (Table 2). All metals except Fe had individual samples (fraction 1 and 2) that exceeded the LEL and the probabilities of an individual street sediment sample (fraction 1 and 2) exceeding the LEL, based on the BestFitTM analysis, are shown in Fig. 6. The more traditional expression of metal levels in Table 2, total concentration, shows that the means

of all metals exceeded the LEL and the means of Cu, Fe, and Mn also exceeded the SEL. The use of total concentration here suggests that there may be a greater environmental problem than actually exists. Nonetheless, the result for Mn is of particular interest since concern recently has been expressed with respect to Mn and human health impacts.



Fig. 5 a–f Kriging analysis showing the spatial distribution of Zn (log10 of microgram per gram) in each chemical fraction (sediment size class <63 μm). The *white lines* represent major roadways and the outline of the Kenilworth sewershed also is overlaid



Inhalation of excessive levels of Mn appears to have neuromotor consequences in adults, producing Parkinson-like effects, and there is emerging evidence of reduced intellectual function and even mortality if children are exposed to high levels of Mn in drinking water (e.g., Wasserman et al. 2006; Weiss 2006; Finkelstein and Jerrett 2007; Hafeman et al. 2007).

3.3 Total concentration from bulk and sediment size-normalized analysis

The total metal concentration determined from the bulk sample analysis as presented by Droppo et al. (2006) and from the summation of sediment size-normalized fractions is shown in Table 1. Results are comparable, although not



Table 2 Mean total concentrations and mean potential bioavailable concentrations (all land uses together) compared to MOEE guidelines (mean potential bioavailability = sum of fractions 1 and 2 = sum of exchangeable and carbonatebound fractions)

Metal	LEL (μ/g)	SEL (μ/g)	Mean total concentration (μ/g)	Mean potential bioavailability (Fr1+Fr2; μg/g)	Range (Fr1+Fr2; μg/g)
Cd	0.6	10	1.85	0.44	0.11–2.6
Cu	16	110	134	9.55	0.10-33.7
Fe	2,100	4,380	60,913	232	10.6-1,118
Mn	460	1,100	3,573	513	127-1,004
Pb	31	250	170	19.8	0.76-411
Zn	120	820	450	126	38.2-256

LEL lowest effect level, SEL severe effect level

identical. Some difference can be expected because of the different approaches to analysis (sediment size fraction vs. bulk sample) but the relative rank of metal concentration by land use was the same for both approaches. For example,

Mn was highest in the industrial area, followed by high-traffic residential and then low-traffic residential for both methods (see Table 1). Interestingly, both SediGraph (gravel, sand, and silt/clay) and sieve fractionation (as per

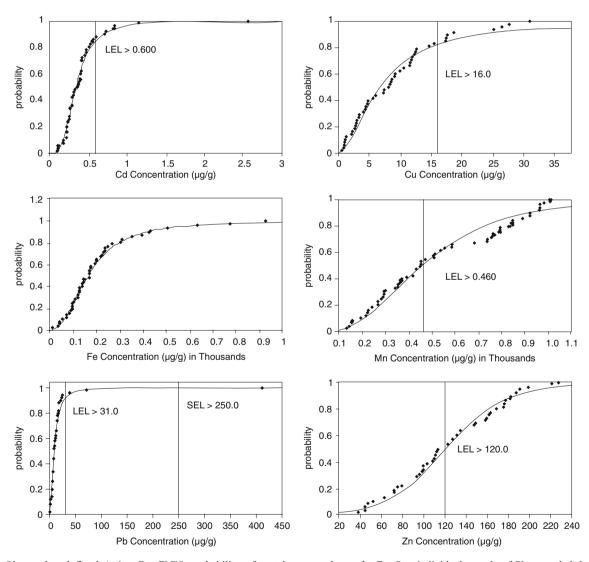


Fig. 6 Observed and fitted (using BestFitTM) probability of metal concentrations exceeding the MOEE lowest effect level (LEL). No individual samples of Fe exceeded the LEL and the LEL therefore is

not shown for Fe. One individual sample of Pb exceeded the MOEE severe effect level (SEL) and both the LEL and SEL are shown



Table 3 Mass loadings of total metals and bioavailable metals (fractions 1 and 2 = sum of exchangeable and carbonate-bound fractions) potentially removed by street sweeping per year

Metal	Minimum load, total concentration, kg ^a	Maximum load, total concentration, kg	Maximum load, bioavailable fraction (Fr1+Fr2), kg	Minimum load, bioavailable fraction (Fr1+Fr2), kg
Cd	0.117	5.73	0.028	1.36
Cu	8.51	415	0.61	29.6
Fe	3,867	188,528	14.7	718
Mn	227	11,059	32.6	1,588
Pb	10.8	526	1.26	61.3
Zn	28.6	1,393	8.0	390

^a Minimum load is based on the assumption of minimum efficiency in particle removal while maximum load is based on the assumption of maximum efficiency of particle removal

size ranges stated in Fig. 3) yielded very similar proportions of each mean size fraction for each land use type. This suggests that differences between land use are related more to the effective metal concentrations and less so to the size distribution.

4 Management implications—potential for metals removal by street sweeping and constructed wetlands

The practice of municipal street cleaning in North America is not new; in fact, the city of New York established a Department of Street Cleaning in 1881 and by 1914 employed 7,153 staff. Most of the street sweeping was done by hand, although machine sweeping had begun by 1914 (Fetherston 1914). Work done in the early 1980s under the US EPA Nationwide Urban Runoff Program indicated that the tested street sweepers were not effective in picking up fine sediment and therefore street sweeping was not a good approach to improving stormwater quality (Sutherland and Jelen 1997). Generally, these sweepers were of the mechanical broom-type design and, since that

time, progress has been made towards improving streetsweeping technology, with regenerative air and vacuum filter-type systems now available. For example, Sutherland and Jelen (1997) found that regenerative air units had removal efficiencies of 32% for particle sizes <63 µm, 71% for particles between 63 and 125 µm, and 94% for particles between 125 and 250 µm. As a result of the improved technology, there seems to be a renewed interest in evaluating street sweeping as an effective stormwater and air quality BMP (e.g., Curtis 2002; Zarriello et al. 2002; Breault et al. 2005; Chang et al. 2005; Schilling 2005; Selbig and Bannerman 2007; Law et al. 2008). Schilling (2005) concluded that street sweeping is cost-effective compared to structural BMPs, particularly when integrated as a component of an overall environmental management plan. However, studies also have shown how difficult it is to directly document improvement to receiving water body quality as the result of sweeping alone (Schilling 2005; Selbig and Bannerman 2007; Law et al. 2008). In part, this seems to be due to the variability of metal levels between different storms and the difficulty of maintaining funding for a long-term monitoring project that would provide



Fig. 7 Open channel leading from CSO to retention pond



Fig. 8 Retention pond that could be configured into a constructed wetland



enough sampling to account for metal levels variability. Chang et al. (2005) concluded that street sweeping, followed by washing, could provide a measurable reduction of total suspended particulate matter in the urban airshed.

A simple calculation of the potential mass of bioavailable and total metals removed from the urban street surface through sweeping can be instructive. The City of Hamilton uses a Tymco DST-6TM (regenerative air) sweeper and has a routine sweeping schedule of once per week. In our calculation, we assume that sweeping is done 40 weeks per year (i.e., is not done during typical snow cover months). Based on the ArcGIS9.2 calculations, the Hamilton study area shown in Figs. 2, 4, and 5 would have 248 km of curb. Applicable data on measured mass of total solids picked up by municipal sweepers are sparse in the literature, but Curtis (2002) reported a range of 6.4-312 kg per curb kilometer for various municipalities in Montgomery County. MD, USA (regenerative air-type sweepers). Pitt et al. (2004) also reported street sediment removal rates within this range. Based on the mean bioavailable concentrations (fractions 1 and 2) summarized in Table 2, the operating conditions for street sweeping in the Hamilton study area and the range of street sediment removal rates reported by Curtis (2002) and Pitt et al. (2004), the estimated total mass of metals removed, on an annual basis, is presented in Table 3. A similar calculation was made for mean total metal concentration and also is presented in Table 3.

The mass removal calculation in Table 3 represents the potential mass of bioavailable metals or total metals diverted from entering a combination of the Hamilton airshed and Hamilton Harbor through CSO discharge. Clearly, when the calculations are based on total metal concentrations, the mass removed is more impressive. The calculation does not explicitly account for the different removal efficiencies by size. As noted by Sutherland and Jelen (1997), the removal efficiency of a regenerative sweeper is lower for particle sizes <63 μm. Droppo et al. (2002) showed that the size of sediment decreased as the street sediment washed off the urban surfaces of the Kenilworth sewershed. The sediment in the CSOs was highly flocculated and had median bulk settling velocities in the 3-7-mm/s range. The CSO flocs incorporate some of the finer mineral sediment from street wash off with organic matter from the sanitary waste. The Kenilworth CSO discharges to an open canal and then into a retention pond before the flow enters the harbor (Figs. 7 and 8). It seems possible that the canal and pond area could be naturalized in a constructed wetland configuration that would optimize removal of sediment in the measured range of settling velocities (e.g., Cappiella et al. 2008). In this way, street sweeping together with naturalized storm water management may provide a benefit to Hamilton Harbor.

5 Conclusions

Significant spatial trends in the levels of metals, with the exception of Cd, were observed in the central area of Hamilton, Ontario, Canada. Mn and Fe levels were associated with a well-defined heavy industrial area that includes large iron- and steel-making operations while Cu and Pb were associated with both the industrial and high-volume traffic areas. Spatial trends in Zn tended to be more associated with high-volume traffic areas. Kriging was an effective method to analyze and visualize these spatial trends.

The street sediment samples were chemically fractionated using a sequential extraction procedure and the relative bioavailability (based on fractions 1 and 2) decreased in the order: Zn > Cd > Mn > Pb > Cu > Fe, which is similar to the order reported in the literature. The sum of fractions 1 and 2 was compared to Ontario guidelines for aquatic sediment and the mean level for Zn and Xn exceeded the lowest effect level. This finding is of particular interest since more recent work has indicated that Xn presents a higher health risk than previously thought.

There has been an increasing focus on implementing both nonstructural and structural BMPs to reduce the impact of stormwater and sewer discharges on receiving waters in North America. Control of street sediment as a fugitive emission to the atmosphere also has received increased attention. The metals and street sediment particle size data presented in this paper could be used to help determine an appropriate combination of BMPs, such as street cleaning and constructed wetlands, to improve environmental quality in the Hamilton region.

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References

Breault RF, Smith KP, Sorenson JR (2005) Residential street-dirt accumulation rates and chemical composition, and removal efficiencies by mechanical- and vacuum-type sweepers. New Bedford, Massachusetts, 2003-04, USGS Scientific Investigations Report 2005-5184

Cappiella K, Fraley-McNeal L, Novotney M, Schueler T (2008) The next generation of stormwater wetlands. Wetlands &Watersheds Article 5, Center for Watershed Protection

Chang Y-M, Chou C-M, Su K-T, Tseng C-H (2005) Effectiveness of street sweeping and washing for controlling ambient TSP. Atmos Environ 39:1891–1902

Corporation P (2005) @RISK advanced risk analysis for spreadsheets. Ithaca, NY

Curtis MC (2002) Street sweeping for pollutant removal. Report, Department of Environmental Protection, Montgomery County, MD



- Droppo IG, Irvine KN, Jaskot C (2002) Flocculation/aggregation of cohesive sediments in the urban continuum: implications for stormwater management. Environ Technol 23:27–41
- Droppo IG, Irvine KN, Curran KJ, Carrigan E, Mayo S, Jaskot C, Trapp B (2006) Understanding the distribution, structure and behaviour of urban sediments and associated contaminants towards improving water management strategies. In: Owens PN, Collins AJ (eds) Soil erosion and sediment redistribution in river catchments. CAB International, Wallingford, pp 272–286
- Ellis JB, Revitt DM, Harrop DO, Beckwith PR (1987) The contribution of highway surfaces to urban stormwater sediments and metals loadings. Sci Total Environ 59:339–349
- U.S. EPA (1995a) Combined Sewer Overflows Guidance for Long-Term Control Plan. U.S. EPA Report, EPA 832-B-95-002
- U.S. EPA (1995b) Combined Sewer Overflows Guidance for Nine Minimum Controls. U.S. EPA Report, EPA 832-B-95-003
- Fetherston JT (1914) Discussion of street cleaning. Proc Acad Polit Sci City N Y 5:187–191
- Field R, Heaney JP, Pitt R (eds) (2000) Innovative urban wet-weather flow management systems. Technomic, Lancaster 535 pp
- Finkelstein MM, Jerrett M (2007) A study of the relationships between Parkinson's disease and markers of traffic-derived and environmental manganese air pollution in two Canadian cities. Environ Res 104:420–432
- Gibson MJ, Farmer JG (1984) Chemical partitioning of trace metal contaminants in urban street dirt. Sci Total Environ 33:49–57
- Hafeman D, Factor-Litvak P, Zhongqi C, van Geen A, Ahsan H (2007) Association between manganese exposure through drinking water and infant mortality in Bangladesh. Environ Health Perspect 115:1107–1112
- Hamilton RS, Revitt DM, Warren RS (1984) Levels and physicochemical associations of Cd, Cu, Pb, and Zn in road sediments. Sci Total Environ 33:59–74
- Harrison RM (1979) Toxic metals in street and household dusts. Sci Total Environ 11:89–97
- Herngren L, Goonetilleke A, Ayoko GA (2006) Analysis of heavy metals in road-deposited sediments. Anal Chim Acta 571:270–278
- Ho YB, Tai KM (1988) Elevated levels of lead and other metals in roadside soil and grass and their use to monitor aerial metal depositions in Hong Kong. Environ Pollut 49:37–51
- Irvine KN, Droppo IG, Murphy TP, Stirrup DM (1998) Annual loading estimates of selected metals and PAHs in CSOs, Hamilton, Ontario, using a continuous PCSWMM approach. In: James W (ed) Advances in modeling the management of stormwater impacts, vol 6. Ann Arbor Press, Ann Arbor, pp 383–398
- Irvine KN, Caruso J, McCorkhill G (2005) Consideration of metals levels in identifying CSO abatement options. Urban Water J 2(3):193–200
- Kok S, Shaw J, Seto P, Weatherbe D (2000) The urban drainage program of Canada's Great Lakes 2000 Cleanup Program. Water Qual Res J Can 35:315–330
- Krantzberg G (1994) Spatial and temporal variability in metal bioavailability and toxicity of sediment from Hamilton Harbour, Lake Ontario. Environ Toxicol Chem 13(10):1685–1698
- Krantzberg G, Boyd D (1992) The biological significance of contaminants in sediment from Hamilton Harbour, Lake Ontario. Environ Toxicol Chem 11(11):1527–1540
- Law NL, Diblasi K, Ghosh U (2008) Deriving reliable pollutant removal rates for municipal street sweeping and storm drain cleanout programs in the Chesapeake Bay Basin. Report, Center for Watershed Protection
- Lee P-K, Yu Y-H, Yun S-T, Mayer B (2005) Metal contamination and solid phase partitioning of metals in urban roadside sediments. Chemosphere 60:672–689
- Legorburu I, Millan E (1986) Trace metals in air, grass and soil in an urban and industrial area in north Spain: impact of a steel factory. Environ Technol Lett 7:643–648

- Li L, Mattu G, McCallum D, Hall K, Chen M (2006) The temporal and spatial dynamics of trace metals in sediments of a highly urbanized watershed. J ASTM Int 3(7):189–200
- Manno E, Varrica D, Dongarra G (2006) Metal distribution in road dust samples collected in an urban area close to a petrochemical plant at Gela, Sicily. Atmos Environ 40:5929–5941
- Miguel AG, Cass GR, Glovsky MM, Weiss J (1999) Allergens in paved road dust and airborne particles. Environ Sci Technol 33:4159–4168
- NWRI (1990) National Water Research Institute certificate of analysis: certified reference material WQB-1; trace metals in sediment. Aquatic Quality Assurance Program, Research and Applications Branch, National Water Research Institute, Burlington
- Ontario Ministry of Environment and Energy (MOEE) (1993) Guidelines for the protection and management of aquatic sediment quality in Ontario. Queen's Printer for Ontario, Toronto. ISBN 0-7729-9248-7
- Paul Theil Associates and Beak Consultants (1991) Regional Municipality of Hamilton-Wentworth pollution control plan. Regional Municipality of Hamilton-Wentworth
- Pitt R, Bannerman R, Sutherland R (2004) The role of street cleaning in stormwater management. In: Water World and Environmental Resources Conference 2004, Proceedings, Environmental and Water Resources Institute of the American Society of Civil Engineers. http://rpitt.eng.ua.edu/Publications/StormwaterTreatability/Street% 20Cleaning%20Pitt%20et%20al%20SLC%202004.pdf
- Pitt R, Bannerman R, Clark S, Williamson D (2005) Sources of pollutants in urban areas (part 1)—older monitoring projects. In: James W, Irvine KN, McBean EA, Pitt RE (eds) Effective modeling of urban water systems, monograph 13. Computational Hydraulics International, Guelph, pp 465–484
- Ramlan MN, Badri MA (1989) Heavy metals in tropical city street dust and roadside soils: a case study of Kuala Lumpur, Malaysia. Environ Technol Lett 10:435–444
- Robertson DJ, Taylor KG (2007) Temporal variability of metal contamination in urban road-deposited sediment in Manchester, UK: implications for urban pollution monitoring. Water Air Soil Pollut 186:209–220
- Schilling JG (2005) Street sweeping—report no. 1. State of the Practice. Report prepared for Ramsey-Washington Metro Watershed District, North St. Paul, MN
- Selbig WR, Bannerman RT (2007) Evaluation of street sweeping as a stormwater-quality-management tool in three residential basins in Madison, Wisconsin. USGS Scientific Investigations Report 2007-5156
- Solomons W, Förstner U (1984) Metals in the hydrocycle. Springer, New York
- Stone M, Droppo IG (1996) Distribution of lead, copper and zinc in size-fractionated river bed sediment in two agricultural catchments of southern Ontario, Canada. Environ Pollut 3:353–362
- Stone M, Marsalek J (1996) Trace metal composition and speciation in street sediment: Sault Ste. Marie, Canada. Water Air Soil Pollut 87:149–169
- Sutherland RA (2002) Comparison between non-residual Al, Co, Cu, Fe, Mn, Ni, Pb and Zn released by a three-step sequential extraction procedure and a dilute hydrochloric acid leach for soil and road deposited sediment. Appl Geochem 17:353–365
- Sutherland RA (2003) Lead in grain size fractions of road-deposited sediment. Environ Pollut 121:229–237
- Sutherland RC, Jelen SL (1997) Contrary to conventional wisdom, street sweeping can be an effective BMP. In: James W (ed) Advances in modeling the management of stormwater impacts, vol 5. Computational Hydraulics International, Guelph, pp 179–190
- Sutherland RA, Tack FMG (2007) Sequential extraction of lead from grain size fractionated river sediments using the optimized BCR procedure. Water Air Soil Pollut 184:269–284



- Sutherland RA, Pearson DG, Ottley CH (2007) Platinum-group elements (Ir, Pd, Pt and Rh) in road-deposited sediments in two urban watersheds, Hawaii. Appl Geochem 22:1485–1501
- Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51:844–850
- Vermette SJ, Irvine KN, Drake JJ (1987) Elemental and size distribution characteristics of urban sediments: Hamilton, Canada. Environ Technol Lett 8:619–634
- Vermette SJ, Irvine KN, Drake JJ (1991) Temporal variability of the elemental composition in urban street dust. Environ Monit Assess 18:69–77
- Wasserman GA, Liu X, Parvez F, Ahsan H, Levy D, Factor-Litvak P, Kline J, van Geen A, Slavkovich V, Lolacono NJ, Cheng Z,
- Zheng Y, Graziano JH (2006) Water manganese exposure and children's intellectual function in Araihazar, Bangladesh. Environ Health Perspect 114:124–129
- Weiss B (2006) Economic implications of manganese neurotoxicity. Neuro Toxicol 27:362–368
- Zarriello P, Breault RF, Weiskel PK (2002) Potential effects of structural controls and street sweeping on stormwater loads to the lower Charles river, Massachusetts. USGS Water-Resources Investigations Report 02-4220
- Zeman AJ, Patterson TS (2003) Characterization and mapping of contaminated sediments, Windermere Arm, Hamilton Harbour, Ontario, Canada. Soil Sediment Contam 12:619–629

