RESEARCH ARTICLE



Urban stormwater runoff pollutant loadings: GIS land use classification vs. sample-based predictions

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Abstract

Cities are growing worldwide with an increase in stormwater quantity and decrease in quality, negatively impacting receiving water bodies. The characterization of stormwater is difficult given its high variability and the typically numerous outfalls to be monitored. However, loadings can be estimated via models and validated using actual outfall monitoring. This study determined stormwater pollutant loadings predicted using eight land-use classifications (i.e., a 'desktop' study) and via an outfall sampling regime (i.e., a 'monitoring' study) for seven stormwater catchment areas in Saskatoon, SK, Canada, where stormwater typically releases directly into the South Saskatchewan River. Pollutants considered were total suspended solids (TSS), chemical oxygen demand (COD), metals, and polycyclic aromatic hydrocarbons. Catchment areas were dominated by single-family residential (39%) and green areas (17%). The largest catchment area, Preston Crossing, was the major source of the predicted annual loadings, such as TSS at 550,000 kg and COD at 265,000 kg. For comparison, the sampled-based estimated loadings for TSS and COD were 362,700 kg and 652,700 kg, respectively. Differences between the average predicted and actual estimations ranged from 29 to 156% for the eight pollutants considered, with averages for the summed pollutants in each catchment area ranging from 48 to 130%. Overall, the assessment and monitoring of stormwater outfalls are needed for the determination of impacts of loadings on the environment and for the subsequent development and implementation of treatment technologies.

Keywords Stormwater runoff \cdot Land-use classification \cdot GIS \cdot Stormwater quality, pollutant emission \cdot Pollutant loads predictions \cdot Polycyclic aromatic hydrocarbons (PAHs)

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Introduction

Urban landscapes are continually modified by human activities, especially in response to increasing populations and urbanization worldwide. The modification of existing landscapes includes the removal of vegetation and replacing it with manufactured impervious surfaces that lead to decreased absorption of precipitation. In addition, recent climate change effects have led to more extreme weather events with increases in precipitation, including both rainfall and snowfall, in many geographic regions. Urbanization also creates more potential sources of pollutants that create higher pollutant concentrations of physical, chemical, and biological origins in stormwater runoff (Baek et al. 2015; Borris et al. 2016; Goonetilleke et al. 2005; Jartun & Pettersen 2010). Historically, in many regions, including areas of Canada, stormwaters are released directly into receiving waters with minimal or no treatment. Urban stormwater runoff is a major contributor of organic, metallic, and other pollutants that degrade receiving water bodies by impacting aquatic organisms and altering the characteristics of the ecosystem (Fraga et al. 2016; Goonetilleke et al. 2005; Järveläinen et al. 2017; Wang et al. 2020; Yufen et al. 2008). Not only do these stormwaters have the potential to negatively impact environmental health, but they can also impact human health for populations within and downstream of urban centers via exposure routes including drinking water, fish/waterfowl consumption, and recreational activities.

Most urban stormwater runoff pollutants have non-point sources originating from both impervious and pervious surfaces (Brezonik & Stadelmann 2002; Lee & Bang 2000; Prestes et al. 2006). Impervious, human-made surface sources may include paved parking lots, streets, driveways, roofs, and sidewalks. Pervious areas may include gardens, bare ground, unpaved parking areas, construction sites, and undeveloped areas which may closely mimic natural landscapes. Various land-use areas of a municipality can contribute to stormwater pollution. These areas have been grouped previously into land-use classifications, including residential, commercial, roadways/highways, agricultural, undeveloped or 'green' areas, light/heavy industrial, and undeveloped areas (Bach et al. 2015; Järveläinen et al. 2017). Thus, the urban environment, anthropogenic activities, and natural processes within each catchment are all key factors in the contamination of stormwater (Jartun et al. 2008; Matos et al. 2015).

The accumulation of pollutants on various urban surfaces and their 'wash-off' during weather events are dependent on climate characteristics such as rainfall intensity and duration, pollutant sources based on land use (Brezonik & Stadelmann 2002; Maniquiz et al. 2010), and the individual catchment-specific characteristics (Borris et al. 2016; Zhang et al. 2015). High intensity and/or long-duration rainfalls lead to significant stormwater volumes that may cause flooding, property damage, and increased erosion of waterways. These rainfall runoffs also carry high pollutant loadings that vary based on the catchment area land uses and total surface areas. For example, residential lawns may contribute phosphorus, nitrogen, and organic matter loadings. Alternatively, highways and roads are sources of petroleum hydrocarbons, sulfur, heavy metals, solids, oil and grease, and litter (Kayhanian et al. 2007; Kim et al. 2005), while commercial and industrial sites generate elevated loads of heavy metals and organic pollutants (Järveläinen et al. 2017). The catchment characteristics are largely dependent on the regional land uses that can vary depending on each individual municipality's topography and stormwater infrastructure. The accurate determination of these stormwater pollutant loadings is difficult and costly for municipalities, given the complexity of these interrelated factors.

Over the past 20 years, stormwater pollutant concentrations and loadings assessment and prediction have been a challenge in urban hydrology (Sakson and Brzezinska 2018). Policies for managing urban runoff are reliant on monitoring studies, stormwater modeling, and extrapolation of information for similar regions (Barbosa et al. 2012). Monitoring studies are often difficult because of the number of stormwater outfalls found in many urbanized areas. For example, the current study city has over 100 stormwater outfalls into the receiving river. Estimation of stormwater pollutant loads from monitoring studies are limited due to: low reliability of load estimates given flow variability, making accurate sampling challenging; the high costs for pollutant sample analysis for a wide range of contaminants; and the lack of resources to collect samples (Haubner and Joeres 1997; Järveläinen et al. 2017). In addition, extensive and longterm sampling studies are required to understand and predict pollutant loadings that are ever-changing because of climate change and urbanization (Sakson & Brzezinska 2018). Fortunately, loadings can be predicted based on modeling using data including rainfall quantity, land uses, surface types, and estimated surface area mass pollutant concentrations (Järveläinen et al. 2017). For example, Brezonik and Stadelmann (2002) found that the total rainfall, drainage area, land use, and impervious area are the most significant variables needed for the predictions. Lastly, previous stormwater data can be useful as a first method for the prediction of pollutant loadings in any region with further model improvements for site-specific variables informed by actual sampling for model validation and testing.

The study of the impacts of the City of Saskatoon (COS) stormwater runoff to the South Saskatchewan River (SSR) in Saskatoon, Saskatchewan, Canada, has been historically limited despite its potential to negatively impact the SSR and downstream municipalities (McLeod et al. 2006). The COS has inadequate historical monitoring data of these outfalls; thus, the application of previously developed model methodologies would be beneficial as a first step to acquire a better understanding of COS stormwater runoff. This modeling can then be compared to sampling-regime data for model validation. Thus, the objectives of the current study are: (i) to delineate land uses for seven large stormwater catchment areas of the COS using GIS; (ii) use previous literature concentration information and COS regional rainfall data to estimate pollutant concentrations from each of these catchments; (iii) to determine which land-use categories may have the greatest impact on catchment-level pollutant loadings; (iv) to estimate the total pollutant loadings from urban runoff of these catchments into the SSR; and (v) to compare model estimated pollutant loadings with sampling-regime data collected during actual rainfall events. The pollutants considered include total suspended solids (TSS), chemical

oxygen demand (COD), metals (Pb, Zn, Cu, Cr, Ni), and polycyclic aromatic hydrocarbons (PAHs).

Materials and methods

Study area

The City of Saskatoon (COS) is located in Saskatchewan, Canada, on the banks of the South Saskatchewan River (SSR) (52° 07' N, 106° 38' W) (Fig. 1). The COS is the largest municipality in Saskatchewan, having a population of 246,376 and a total area of 228.1 km² (Science and Economic Development 2016; Statistics Canada 2016). The climate is continental, dry, and sunnier than average in Canada, averaging 2,268 h of sunshine annually. The average annual precipitation in the region is 340.4 mm, with summer being the wettest season. Thunderstorms are common in the summer months and can be severe with torrential rain, hail, high winds, intense lightning, and tornadoes (Environment Canada 2016). Furthermore, long dry periods between successive summer storms create the possibility for large pollutant mass accumulation in catchment areas. In winter, snow cover normally lasts from October to March and has a large surface area to volume ratio, which has a high capability of accumulating pollutants. Moreover, snow in this region may accumulate compounds that rain will not, such as volatile organics. Despite having different characteristics than rainfall, the determination of the impacts of snowmelt pollutant contamination are not included in this project but will be considered in future research by our group.

The COS has separate stormwater sewers (i.e., not connected with sanitary sewer systems) with over 100 outfalls that have historically been released directly into the SSR without treatment. Of these outfalls, 14 outfalls have catchment areas greater than 100 ha (1 km²), with seven of these



Fig. 1 The seven stormwater catchment areas of interest for the current study within the City of Saskatoon (modified based on City of Saskatoon created maps). Stars (*) indicate the eight rain gauge stations for the City of Saskatoon (52°07′N 106°38′W)

catchment areas with varying land uses assessed for this study (Fig. 1). These seven catchment areas also overlap with some areas considered in previous historical studies (e.g., McLeod et al. 2006; Codling et al. 2020) of the COS, which will allow for direct comparisons between current and historical data (Table 1). These large catchment areas represent a total of about 40% of the overall COS area.

GIS land-use classification predictions

Geographic Information System (GIS) can be used to classify catchment areas by individual land uses. This classification can assist in the estimation of non-point source pollution loads with a level of accuracy that is suitable for potential stormwater infrastructure planning purposes (Adamus and Bergman 1995; Strager et al. 2010; Ventura and Kim 1993). The seven catchment areas used currently have been delineated by the COS based on the area topography and knowledge of the existing stormwater infrastructure (Fig. 1). Each of these catchment areas was divided into land-use classes based on land-use classifications (Table 2) following Järveläinen et al. (2017). To fit the land-use classifications, the COS city center was combined into commercial areas, and all single-detached buildings were included as single-family residential. Land uses were defined by Google

 Table 1
 Major City of Saskatoon COS stormwater catchment areas and their general characteristics

Catchment Name	Catchment Area (km ²)	Relative Area (% of COS)	Primary Catchment Type
Preston Crossing	33.2	14.6	University/Hospital
Dog Park	26.8	11.8	Undeveloped
Weir/33rd Street	10.1	4.40	Light Industrial
Taylor Street	8.47	3.71	Older Residential
Spadina/Sturgeon	7.03	3.08	Light Industrial
Whiteswan/ WWTP	3.92	1.72	Residential
Avenue B South	1.20	0.53	Commercial
Total	90.7	39.8	

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Earth Pro and ArcGIS based on the most recent information available from the COS. Land uses were manually delineated with individual land uses summed in each catchment to determine the total area of each land-use classification in that catchment area. Five random areas for each land use were selected and the roads delineated for determining percentage areas of roads/highways. (This information was not included in the COS data.) An example of this delineation is included in Supporting Information (Figure S1). An example of the overall land-use delineation for the largest catchment area, Preston Crossing, is presented in Fig. 2, with the remaining catchment areas included in the SI (Figure S2a-f).

Rainfall, Runoff Coefficients, and SMC Values

The COS collects rainfall data from eight rain gauges (Fig. 1). Monthly rainfall data from six of these rain gauges were used currently to estimate individual catchment stormwater runoff volumes and, in conjunction with literature areal pollutant loading data, resultant pollutant concentrations. Saskatoon's rainfalls are often localized (COS 2016a, b); thus, rain gauges closest/within each catchment area were used for the determination of rainfall volumes.

Each rainfall event's individual pollutant concentration can be used to calculate an event mean concentration (EMC) by dividing the total pollutant mass by the total event volume. The site mean concentration (SMC) is the geometric mean of multiple rainfall events' EMC over a time interval (Charbeneau and Barrett 1998; US EPA 1983). This interval was 6 months, April through September, for the current study, given that this is the typical rainfall season for the COS. The SMC is considered the most accurate measure of the average pollutant concentrations as it is measured as event-volume-weighted mean values of EMCs (Järveläinen et al. 2017). There is no existing SMC data for the current study catchment areas; thus, SMC values were considered based on averages of land-use classifications found in previous studies, including Melanen (1981), Mitchell (2005), Nordeidet et al. (2004), and Järveläinen et al. (2017) (Table 3).

Table 2The land-useclassification used based onJärveläinen et al. (2017) andreferences therein. Runoffcoefficients (CR) considered inthe current study follow City ofSaskatoon (COS) guidelines foreach land-use class (COS 2018)

Land-use class	Acronym	CR	Description
Single-family Residential	SR	0.30	Single dwelling house
Multi-family Residential	MR	0.60	Multiple separate housing units within building
Roads	R	0.95	With average traffic less than 15,000 vehicles/day
Highways	HW	0.95	With average traffic more than 15,000 vehicles/day
Commercial	СМ	0.60	Downtown, central business district, shopping center, university, hospital etc
Industrial	IN	0.60	Industrial area
Green	GR	0.10	Parks, forests, meadows and any other undeveloped area
Agricultural	AG	0.05	Cultivated area



Fig. 2 An example land-use delineation for Preston Crossing, which is the largest City of Saskatoon catchment area. Land-use classifications are presented in Table 2, with areas in the current figure being numbered starting from 1. The other six study catchment area land-

use delineations are included in Supporting Information (S2a-f). The 'Road' land use is not shown in this figure to simplify viewing of the other areas, please see Sect. 2.2 for information on this land use

A runoff coefficient (CR) is the ratio of the total depth of runoff to the total depth of rainfall which is used to estimate direct runoff volumes during a rainfall event (Mahmoud et al. 2014). Land use is a key factor to impact and help determine relevant runoff coefficients (Sajikumar and Remya 2015). The COS has determined CRs for each of the current land-use classifications previously, with values presented in Table 2 (COS 2018). These values were used directly without modification in the estimation of rainfall runoffs for the current study.

Estimation of Pollutant Loads and Monitoring Program Data Requirements

Monthly unit area loads and monthly pollutant export for the six-month period were calculated for individual pollutants

for each land-use class within all catchments areas following the modeling methodology of Novonty, 2003. Briefly, Eqs. (1) and (2) were used for monthly pollutant load calculations as follows.

$$L_{ua} = (CR)P(SMC) \tag{1}$$

where L_{ua} (kg/km²) is the monthly unit area load, *CR* (dimensionless) is the averaged land-use runoff coefficient as presented in Table 2, *P* (mm) is the monthly precipitation depth, and *SMC* (mg/L) is the characteristic event-volume-weighted SMC.

$$L_{tot} = L_{ua}A \tag{2}$$

where L_{tot} (kg) is the monthly pollutant export rate, and A (km²) is the total area of the individual land-use class. Total

Table 3 Flow weighted site mean concentration (SMC) values for a variety of parameters for the different land-use classes. These values represent the average and standard deviation (SD) from studies

including Melanen (1981), Mitchell (2005), Nordeidet et al. (2004) and Järveläinen et al. (2017). Note that the PAHs were only measured by Järveläinen et al. (2017) and have no standard deviation values

Land-use class	Source	TSS (mg/L)	COD (mg/L)	Pb (µg/L)	$Zn \ (\mu g/L)$	Cu (µg/L)	$Cr (\mu g/L)$	Ni (µg/L)	PAHs (µg/L)
Single-family Residential	Average	100	57	60	144	32	4.9	16.5	0.4
	SD	81	36	50	109	17.5	3.5	19	0
Multi-family Residential	Average	118	68	73	252	39.5	13	21	0.6
	SD	47	45	71	87	8	8	13	0
Roads	Average	271	120	114	237	55	20	29	0.8
	SD	175	62	117	42	16	17	2	0
Highways	Average	288	117	166	327	64	10	15	1.4
	SD	148	70	139	173	31	4	21	0
Commercial	Average	194	91	145	260	84	14	24	0.6
	SD	160	61	140	136	71	9	8	0
Industrial	Average	194	91	145	260	84	14	24	0.6
	SD	160	61	140	136	71	9	8	0
Green	Average	84	38	35	116	19	7	15	0
	SD	61	2.8	30	110	12.5	0	0	0
Agricultural	Average	84	38	35	116	19	7	15	0
	SD	61	2.8	30	110	12.5	0	0	0

loadings for the year were the sum of the individual month L_{tot} values. Unit area calculations (kg/km²) were determined by dividing the total loadings by the individual catchment area.

Following the calculation of pollutant loadings, the optimum number of land-use classes required to accurately estimate annual pollutant loads within the COS was calculated for each catchment using marginal benefit analysis following Stenstrom and Strecker (1993). Briefly, the individual pollutant loadings for each land-use class were summed and used to determine the land use that has the highest weighted impact on the overall loading. The land-use classes were then ordered from highest loadings to lowest loadings for an individual pollutant and the cumulative mass discharge percentage calculated and plotted. Each land use can contribute less than 100% of the cumulative mass with the total summed mass equaling 100% when all eight land uses are considered. Further discussion will be included below. This analysis will be beneficial in the future to best inform the monitoring program strategy and focus sampling and remediation efforts to specific land-use classification areas.

Sample-Based Predictions

Stormwater samples were collected at each of the sevencatchment area stormwater outfall locations during four rainfall events on 3 July, 10 July, 13 August, and 26 August in the summer of 2018. Samples taken were 'grab' samples with a number of samples taken from the outfall resulting in a single 'composite' sample used for analysis. Outfalls were sampled as soon as possible when rainfall commenced with two teams of researchers visiting the seven outfalls. Installation of composite samplers in these locations was not an option due to cost, lack of readily available power, and unavailable 'secure' storage for the outfalls being sampled. Physicochemical measurements at each sampling included temperature (°C), pH, total dissolved solids (TDS, mg/L), and electrical conductivity (EC, µs/cm). Water samples (4 L) were taken directly from the stormwater outfalls and placed into glass containers with PTFE-lined septa before being transported to the laboratory. Analyses for each of the samples included total suspended solids (TSS), chemical oxygen demand (COD), metals (Pb, Zn, Cu, Cr, Ni), and polycyclic aromatic hydrocarbons (PAHs). The TSS and COD analyses followed the relevant Standard Methods for the Examination of Water and Wastewater (APHA 2017). For metals, 100 mL samples were filtered through 0.45 µm diameter acid-washed membrane filters, acidified using nitric acid (pH < 2), and stored in Nalgene bottles (125 mL) at 4 °C until analyzed. Metals were identified using inductively coupled plasma mass spectrometry (ICP-MS, Thermo X Series II ICP-MS, Thermo-Scientific, MA USA).

For PAHs, 1 L samples were filtered through 0.45-µm-diameter acid-washed membrane filters (WhatmanTM 934-AHTM glass microfiber filters) and concentrated using pre-conditioned HLB cartridges (Walters, Milford, OH USA). After filtration, 2 mL of chloroform was added per 1 L of sample as a preservative, with the samples stored in amber glass bottles at 4 °C prior to extraction. A deuterium-labelled internal standard mix (500 mg/L of acenaphthene-d10, chrysene-d12, and phenanthrene-d10 in acetone) provided by Sigma-Aldrich (Oakville, ON) was added to the sample at a $10 \,\mu$ L/L ratio. Before sample addition, Waters Oasis HLB 500 mg extraction columns were pre-conditioned using 3 mL dimethylene chloride (DCM), 3 mL methanol (LC-MS grade), and 3 mL 18.2 MΩ-cm ultrapure water (EMD Milli-Pore Synergy® system, Etobicoke, ON). Up to 500 mL of each SM sample was vacuum-extracted through the column at a rate of 1 drop/second. After extraction, the column was washed with 3 mL of 5% methanol in water and air-dried with suction for up to 30 min. Columns were eluted twice with 5 mL of DCM and once with 5 mL of methanol. The eluate was collected in glass vials and reduced to near-dryness under nitrogen and reconstituted in 0.5 mL nonane. The reconstituted sample was added to a gas chromatography vial and stored at 4 °C.

Samples were analyzed for PAHs using gas chromatography-mass spectrometry (GC–MS) using a Thermo Scientific Trace 1300 or 1310 gas chromatograph coupled with a Thermo ISQ 7000 single quadrupole or a Thermo QExactive quadrupole-Orbitrap hybrid mass spectrometer, respectively. Helium (99.999% purity) was used as the carrier gas to separate the PAHs on an Agilent DB-5 ms (60 m×250 μ m I.D., film thickness 0.1 μ m) fused silica capillary column. Both instruments were operated in full scan mode, and data were analyzed using an isotope-dilution workflow, i.e., areas of target compounds were normalized to the areas of recovered deuterium-labelled standards. A seven-point calibration curve along with extraction and solvent blanks was run with each batch of samples. Limits of detection and quantification are included in Table S1.

Calculation of Pollutant Loads

Seasonal pollutant loadings were calculated based on the following equation by Legret and Pagotto (1999):

$$L = \frac{P}{\sum P_e} \frac{V}{\sum V_e} \sum L_e \tag{3}$$

where L (kg) is the seasonal pollutant load, P (mm) represents the seasonal precipitation, P_e (mm) is the precipitation during each storm event, V (m³) is the seasonal runoff volume, V_e (m³) is the runoff volume computed for each storm event, and L_e is the pollutant load for each individual storm event. The pollutant load for each storm event (L_e) was calculated as:

$$L_e = cV_e \tag{4}$$

where *c* represents the mean concentration of the pollutant (mg/m^3) for each runoff sample. V_e was calculated via:

$$V_e = P_e \sum (A(CR)) \tag{5}$$

where $A(m^2)$ is the drainage area per land use and CR is the runoff coefficient for each land use.

Results and discussion

Land-use analysis

Each of the seven catchment areas was divided into eight land-use classifications using GIS with the largest catchment (33.2 km², 14.6% of COS) shown as an example for Preston Crossing (Fig. 2) and the remaining catchments included in the SI (Figure S2a-f). Each of these catchment areas has unique land use; thus, the summation of each of the landuse classifications for each individual catchment area is a simpler metric for comparative purposes, as presented in Fig. 3a. The overall land-use classification percentages for the COS were determined based on the summation of all land uses for the individual catchment areas, as shown in Fig. 3b.

Overall, each of the individual catchment areas was typically dominated by a single land-use type (41–71%). The Taylor Street, Preston Crossing, and Whiteswan/WWTP catchment areas were mostly single-family residential (SR) areas from 47–71% (Fig. 3a). The Weir/33rd Street and Spadina/Sturgeon areas had large industrial (IN) areas from 41–45%. The Dog Park area was mostly green (GN) space at 66%, and the Avenue B S area was mostly commercial (CM) at 62%. These classifications were largely in agreement with the historic COS classification as University/ Hospital (or commercial) is no longer accurate as this area is now dominated by SR areas. This highlights the need for up-to-date land-use information for urban centers that are constantly being modified and growing over time.

The most common land uses for the COS were singlefamily residential (39%), followed by green, commercial, and industrial with 17%, 13%, and 12%, respectively (Fig. 3b). Overall, multi-family residential, roads, and highways were found in every catchment with areas less than 10% overall, while agricultural land use was available only in a few catchments for a total of 3% of the total study areas. For comparison, Bannerman et al. (1996) found 47% residential area, 8% commercial area, 6% industrial area, and 20% of combined green and agricultural area in Milwaukee, Wisconsin, USA. Luck and Wu (2002) found similar results with approximately 35% of various residential areas within the city of Arizona, NV, USA. In contrast, Järveläinen et al. (2017) found undeveloped green areas dominated 58% of the land area for the cities of Lahti and Espoo in Finland.



Fig. 3 Distribution of land-use classes for (a) individual study catchment areas and (b) sum of all seven study catchment areas

Generally, various catchment areas in cities are dominated by different types of land uses, which makes the averaging of city-scale monitoring of stormwater data resulting in high uncertainty (Järveläinen et al. 2017). For monitoring, and subsequent potential treatment technology implementation, the use of individual catchment area information will be of most interest in planning purposes. Additionally, the separation of catchment areas into various land uses may be useful for informing monitoring and mitigation decisions, as discussed below in the marginal benefits analysis section.

GIS information can be useful for urban centers to determine land uses and topography that can be used in conjunction with precipitation data to propose stormwater remediation strategies, programs, and policies (Chinen et al. 2016; Wong et al. 1997). For example, land-use data and rainfall-runoff relationship models have been coupled with pollutant loading coefficients for assessing runoff volumes and associated pollutant loadings in other regions (Haubner and Joeres 1996; Jato-Espino et al. 2016). Land use is the dominant metric for consideration of non-point source pollution that varies widely based on land uses, including impervious surfaces, vehicles, industrial debris, leaf and animal litter, and others while also considering factors such as slope and soils, and hydrological and meteorological characteristics of an area (Ventura and Kim 1993).

Land-use site mean concentration (SMC) values

Overall, the predicted SMC concentrations were highest for the roads (R), highways (HW), commercial (CM), and industrial (IN) areas for TSS (194–288 mg/L) and COD (92–120 mg/L). This is expected due to the presence of vehicles that are sources of solids through wear-and-tear items, including tires, particulate emissions from internal combustion processes, and from leaking of oils and gases. High availability of solids will lead to increased stormwater COD levels given the presence of organic materials as part of the TSS. In comparison, Bannerman et al. (1996) found urban Milwaukee areas had similar SMC concentrations of TSS (237 mg/L) and COD (69 mg/L). The variety of studies across geographic locations showing similar results indicate that the use of these estimates currently as the first prediction for COS is a reasonable approximation for comparison to initial sampling data. As for TSS and COD, the highest SMC concentrations for all metals (<10 to 330 μ g/L) and PAHs $(0.4-1.4 \mu g/L)$ were generally produced from roads (R), highways (HW), commercial (CM), and industrial (IN) areas (Table 3). This is expected given vehicles are the predominant sources of metals and hydrocarbons in urban areas from vehicle parts and components, tire wear, fuel, and lubricating oils, asphalt pavement, and general road metal structures (Barbosa et al. 2012). As would be expected, green (GR) and agricultural (AG) areas had the lowest concentrations for these pollutants.

GIS Land-use pollutant loadings predictions

The above-calculated SMC concentrations were combined with measured COS rainfall data to determine predicted loadings into the SSR from the seven catchment areas representing about 40% of the COS total area (Fig. 4a-h).

Preston Crossing is predicted to be the dominant source of TSS and COD loadings to the SSR at approximately 550,000 kg and 265,000 kg for the summer season, respectively (Fig. 4a-b). These loadings represent approximately 42-44% of the total COS loadings of 1,305,600 kg and 626,400 kg, respectively. The loadings are marginally higher than expected based on area, as Preston Crossing represents only 37% of the COS study area. Taylor Street, Dog Park, Weir/33rd Street, and Spadina/Sturgeon had similar loadings levels that were at least 50% lower than the Preston Crossing catchment, while Avenue B S and Whiteswan/WWTP had the lowest loadings. Unlike Preston Crossing, the loadings for Taylor Street (12.3-14.0%), Weir/33rd Street (14.9%-18.8%), and Spadina/Sturgeon (8.8-10.5%) were all higher than expected based on their overall areas (9.3%, 11.0%, and 7.7%, respectively), while the Dog Park loadings of 11.0–12.6% were low given that it covers 29.6% of the COS area. Clearly, land uses in these areas impact the predicted (and actual) loading of these pollutants into the SSR, with the primary catchment types of industrial areas having the highest relative loadings.

A similar pattern as TSS and COD is shown for the remaining pollutants, including all metals and PAHs (Fig. 4c-h). Although each of these catchments has unique



Fig. 4 Total predicted based on GIS analysis and total estimated pollutant loads based on actual samples (kg) from each COS study catchment area to the South Saskatchewan River for (a) TSS; (b) COD; (c) Pb; (d) Zn; (e) Cu; (f) Cr; (g) Ni; and (h) PAHs



Fig. 4 (continued)

combinations of land uses, the total area of each was the dominant driver of the pollutant loadings. As shown in Table 1, the Preston Crossing area is much larger (33.2 km^2) than most of the other areas (3.92 to 10.1 km²) with the exception of the Dog Park (26.8 km²). The Dog Park area is unique as it is a largely undeveloped park area; thus, pollutant loadings from this area would be expected to be low. The smallest area of Avenue B S (1.20 km²), dominated by commercial usage, had total loadings around those of the single-family residential Whiteswan/WWTP area that was more than three times the area (3.92 km^2) , indicating that commercial areas can have large total pollutant loadings even over small areas. Similarly, Mulcahy (1990) found that commercial and industrial land uses contribute proportionally more pollutants than urban open space, parks, and lowdensity residential land uses.

Calculation of the loadings per unit area normalizes the loadings for each land-use classification and allows for the extrapolation and comparison of data to other COS catchments, as well as to other regions (Figure S3a-h), regardless of the catchment area overall size given that the loadings are expected to be linearly scalable. The use of only the largest catchments in the current study was done given that these outfalls will be considered in the future for implementation of treatment technologies given that they produce the highest loadings into the SSR. Clearly, the commercial dominant area Avenue B S produced the highest unit area loads for all pollutants, including TSS of 31,460 kg/m², COD of 14,480 kg/m², metals ranging from 2 to 29 kg/m², and PAHs of 0.1 kg/m². In contrast, the green area of the Dog Park contributed the lowest unit area loadings, including TSS of 5,371 kg/m², COD of 2,630 kg/m², metals ranging from < 1to 7 kg/m², and PAHs of 0.01 kg/m². The next highest loading rates were for the dominant industrial areas of Weir/33rd Street and Spadina/Sturgeon, while the remaining residential dominant catchment loadings were lower for all pollutants. McLeod et al. (2006) determined annual TSS and COD loadings for four of the same catchments in the current study, including Taylor Street, Avenue B S, Spadina/Sturgeon (Sturgeon), and Whiteswan/WWTP (Silverwood). Their loadings for Avenue B S were 21,200 kg/m² and 7,300 kg/ m^2 , respectively. It should be noted that the McLeod et al. (2006) results were determined via sampling of stormwater outfalls in contrast to these estimations using only previous SMCs and rainfall data. In general, the currently determined loadings were higher than those calculated by McLeod et al. (2006) but were within a reasonable 2X range of each other.

Sample-based prediction

The average pollutant concentrations for the seven catchment areas sampled during four rainfall events in the summer of 2018 are shown in Table 4. Overall, the Dog Park, Whiteswan/WWTP, Spadina/Sturgeon, and Weir/33rd
 Table 4
 Average and standard deviation (SD) of all measured pollutants sampled in four rainfall events during summer 2018. Note:

 The data presented are analytical standard deviations as only a single

composite sample was taken from stormwater outfalls. '- ' indicates below detection limits

Catchment Name	Source	TSS (mg/L)	COD (mg/L)	Pb (µg/L)	$Zn \ (\mu g/L)$	Cu (µg/L)	$Cr(\mu g/L)$	Ni (µg/L)	PAHs (µg/L)
Taylor Street	Average	43	175	144	161	22	-	8	2.9
	SD	68	159	98	122	7	-	2	2.1
Preston Crossing	Average	147	265	93	118	25	-	7	1.7
	SD	165	105	89	73	6	-	2	1.5
Dog Park	Average	193	340	58	169	36	14	12	2.7
	SD	96	198	90	86	16	2	11	1.6
Avenue B S	Average	87	153	165	97	81	-	11	0.9
	SD	161	139	145	46	61	-	7	0.9
Weir/33rd Street	Average	167	178	186	164	31	9	9	0.4
	SD	305	120	95	126	15	-	3	0.8
Spadina/Sturgeon	Average	151	351	201	150	17	9	7	0.5
	SD	279	196	220	89	11	-	2	0.5
Whiteswan/WWTP	Average	46	493	54	162	60	16	12	2.9
	SD	44	352	49	32	62	-	7	2.5
OVERALL	Average	119	279	129	146	39	12	9	1.7
	SD	160	181	112	82	25	2	5	1.4

SD30312093126Spadina/SturgeonAverage151351201150SD27919622089Whiteswan/WWTPAverage4649354162SD443524932OVERALLAverage119279129146SD16018111282Street outfalls had the highest concentrations with seven,
six, five, and four pollutant concentrations over the average
values, respectively, out of the eight pollutants measured.
The largest catchment area, Preston Crossing, had only one
measurement above the average with 147 mg/L TSS. The
remaining two catchments, Taylor Street and Avenue B S,
had two measurements each above the average (Table 4).Weir/ 33^{rh} The sample-based loadings predictions to the SSR deter-b). This y

values, respectively, out of the eight pollutants measured. The largest catchment area, Preston Crossing, had only one measurement above the average with 147 mg/L TSS. The remaining two catchments, Taylor Street and Avenue B S, had two measurements each above the average (Table 4). The sample-based loadings predictions to the SSR determined via Table 4 concentrations are shown in Fig. 4a-h. The Preston Crossing area dominated the TSS and COD actual loadings with 362,700 kg and 652,700 kg, respectively (Fig. 4a-b). These loadings represent approximately 42 and 43% of the total COS loadings of 835,700 kg and 1,568,400 kg, respectively. The loadings are marginally higher than expected based on the area given that Preston Crossing represents 37% of the COS study area. The Dog Park, Weir/33rd Street, and Spadina/Sturgeon had total actual loadings that were at least 50% lower than the Preston Crossing catchment, while Taylor Street, Avenue B S, and Whiteswan/WWTP had the lowest loadings. Similar to Preston Crossing, the Weir/33rd Street (20% and 12%) and Spadina/Sturgeon loadings (11% and 13%) were higher than expected based on their relative area (11% and 8% of COS), while the Dog Park loadings (20% and 18%) were lower than expected based on its area (30% of COS). Metals and PAHs actual loadings were generally highest for Preston Crossing given its larger area (Fig. 4c-h). All loadings for Preston Crossing were about as would be expected based on its total area. The next highest metals loadings were found in the Dog Park, Spadina/Sturgeon, and Weir/33rd Street outfalls,

with the Taylor Street, Whiteswan/WWTP, and Avenue B S having the lowest actual loadings. Interestingly for the PAHs, the Taylor Street and Dog Park loadings were highest amongst the remaining outfalls.

The actual areal loading (kg/m²) values are shown in Figure S3a-h. The TSS and COD loadings were highest for the Weir/33rd Street and Spadina/Sturgeon outfalls (Fig. S3ab). This would be expected given that both of these catchments are primarily considered to be light industrial areas (Table 1). Interestingly, there does not appear to be a consistent actual loading trend for the metals (Fig. S3c-g) from the catchment areas; thus, land use does not appear to be impacting actual metals loadings from COS catchment areas. For the PAHs, the Taylor Street catchment area had the highest loadings at 0.24 kg/m², which was unexpected given that it is classified as older residential (Table 1). Interestingly, the other residential area of Whiteswan/WWTP also had high PAHs loadings. Reasons for these higher loadings in residential areas may be attributed to the greater number of vehicles in these locations that may be leaking oil/gas into stormwater sewers.

Comparison of GIS vs. sample-based predictions

Although there are many possibilities in which to compare the GIS and sample-based loadings presented in Sects. 3.3 and 3.4, the simplest comparison is via percentage difference (%) between the predicted (GIS) and actual (Sample) estimated loads as presented in Table 5. Overall, the average predicted and actual estimations ranged from 29 to Table 5 Percentage difference (%) between predicted and actual estimated loads for seven catchments sampled during 2018. Positive values indicate predictions were greater than actual loadings, while negative values indicate predictions were less than actual loadings. Averages are calculated using absolute values and are presented in bold

Catchment Name	TSS	COD	Pb	Zn	Cu	Cr	Ni	PAHs	Avg
Taylor Street	445	-36	-14	67	167	-	238	-70	130
Preston Crossing	52	-59	42	143	160	-	269	-49	96
Dog Park	-11	-75	54	33	29	-12	92	-76	48
Avenue B S	253	-7	22	290	33	-	220	9	104
Weir/33rd Street	43	-37	-10	89	200	82	211	97	96
Spadina/Sturgeon	51	-68	-22	99	389	65	281	42	127
Whiteswan/WWTP	238	-83	56	30	-27	-40	93	-78	80
Average	156	52	31	107	144	29	201	61	

156% for the eight pollutants considered, with averages for the summed pollutants in each catchment area ranging from 48 to 130%. Given that the GIS data relied only upon 'desktop' analyses, the agreement between these two estimated loads calculations was quite reasonable overall. As would be expected, the range for the individual pollutants for each individual catchment shows a wider range of differences ranging from -83% (COD for Whiteswan/WWTP) to 445% (TSS for Taylor Street).

Both estimations have benefits and drawbacks that impact their ability to determine pollutant loadings accurately. The GIS-based estimations are dependent on the accuracy of land-use data, areal pollutant loadings, and measured rainfall data. However, these estimations benefit from the simplicity of determining loadings without having to take field samples on a regular basis. The actual sampling estimations are dependent on sampling methodology (grab vs. composite samples), the spatiotemporal sampling regime, and the human resources needed to collect and process samples. However, actual samples are the most accurate for the determination of loadings. Overall, a combination of GIS-based estimations coupled with sampling validation would be a useful methodology to predict the COS pollutant loadings into the SSR.

 Table 6
 Results of marginal benefit analysis for the various pollutants

Data Requirements for Monitoring

The marginal benefits plots for TSS, COD, BOD, TN, TP, individual metals, and PAHs are presented in Figure S3a-i. The goal of the marginal benefits analysis is to capture the highest amount of cumulative mass information while limiting the total number of areas needing to be monitored for each individual pollutant. Thus, the random monitoring line would indicate all eight land uses could incrementally, linearly, be used to calculate 100% of the cumulative pollutant loadings. However, the optimized monitoring lines indicate that some of the land uses are more important to monitor and would be better used for a more focused monitoring strategy for individual pollutants. Essentially, the larger the distance between the two lines, the fewer land uses would need to be monitored. The direct interpretation of these figures is difficult; thus, the results are summarized in Table 6 for a more straightforward comparison between the individual pollutants and land-use classifications. Overall, three or four land uses could be considered to achieve > 60% of the coverage needed for optimal monitoring, with some pollutants reaching > 70% coverage. The most important land uses were single-family residential (SR), commercial (CM), industrial (IN), highways (HW), and roads (R) which were needed for 13, 12, nine, five, and five pollutant assessments

	6 ,	1		
Parameter	Optimum number of moni- tored land uses	Coverage (%) achieved with optimal monitoring	Optimal land uses to monitor	Number of land uses needed for 80% cover- age
TSS	4	74	SR, R, CM, HW	5
COD	4	76	SR, CM, R, IN	5
BOD	3	65	SR, R, HW	5
Pb	3	62	CM, SR, IN	4
Zn	4	72	SR, CM, IN, HW	5
Cu	3	67	CM, IN, SR	4
Ni	3	62	SR, CM, R	5
Cr	3	61	R, CM, IN	5
PAHs	3	61	SR, HW, CM	5

(total of 14). The multi-family residential (MR), green (GR), and agricultural (AG) land uses were not needed for any of the optimizations. As would be expected, to achieve > 80%coverage, the former five land uses were typically needed (12 of 14 cases) to be monitored. Overall, multi-family residential (MR), green (GR), and agriculture (AG) land-use classes were not necessary to get 80% benefit for any pollutants. For comparison, Järveläinen et al. (2017) found two to four land-use classes were needed for optimal monitoring (>60%), while three to six land-use classes for 80% coverage of monitoring. Overall, this analysis would indicate that monitoring studies could be easily optimized based on land uses for the COS, and a similar methodology would be useful for informing monitoring decisions in other areas. This information would also be useful for informing decisions regarding the implementation of stormwater mitigation measures that can be tailored toward the most important land uses rather than for the entire catchment areas.

Conclusions

The determination of stormwater outfall pollutant loadings into receiving water bodies is a difficult task. Loadings can be estimated via models developed via previous research and tested/validated using actual outfall monitoring. Actual loadings may also be estimated via sampling regimes of stormwater outfalls. This study determined stormwater pollutant loadings predicted using eight land-use classifications (i.e., a 'desktop' study) and via a seasonal outfall sampling regime (i.e., a 'monitoring' study) for seven stormwater catchment areas in the City of Saskatoon (COS) that releases stormwater into the South Saskatchewan River (SSR). Both methods of predicting pollutant loadings have benefits and drawbacks that limit their individual abilities to determine accurate loadings. Preston Crossing and Dog Park catchment areas are the largest in Saskatoon, however, have quite different land uses with Preston Crossing being mostly single-family residential, and Dog Park is dominated by green area. Overall, Preston Crossing loadings into the SSR were highest for both predicted and actual estimates based on the land uses and the overall size of the catchment as compared to others in Saskatoon. The predicted and actual estimates were in reasonable agreement for pollutants with a range of 29% to 156% for the eight pollutants considered, with averages for the summed pollutants in each catchment area ranging from 48 to 130%. However, future work including a parallel study determining catchment-specific site mean concentrations (SMCs) and stormwater outfall comprehensive sampling using composite samplers would be valuable in improving the accuracy of the predictions.

Overall, the assessment and monitoring of stormwater outfalls are needed for the determination of impacts of loadings on the environment and for the subsequent development and implementation of treatment technologies. Monitoring of outfalls is often difficult due to the stochastic nature of rainfall events, large number of outfalls, and time and cost of sampling events. This study shows an approach to estimate pollutant loadings as a first approximation using modeling that can then be tested and validated. The model can then be modified, tested, and validated to help inform future stormwater monitoring and treatment consideration both in the COS and in other regions worldwide.

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Authors contributions AA, SR, and NB contributed to all research fieldwork and sample analyses. AA performed GIS-related calculations and created the first draft of this manuscript. MH and MB oversaw the PAH sample analyses. All authors contributed to the manuscript writing and editing and have read and approved the final manuscript.

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Declarations

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