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ENVIRONMENTAL IMPACT STATEMENT

Combined sewer overflows (CSOs) are well known to be a major source of contaminants and to degrade the quality of the receiving waters. As contaminant concentrations vary widely during CSO events, loads are expected to vary as well. This study aims to assess the load variations of wastewater micropollutants, microbiological and physico-chemical contaminants during events and among seasons (including the snowmelt period). The temporal variability of the contributions of wastewater versus the combination of stormwater and sewer deposit resuspension was evaluated in order to assess their impacts on potential CSO treatment options.

Temporal analysis of *E. coli*, TSS and wastewater micropollutant loads from combined sewer overflows: implications for management

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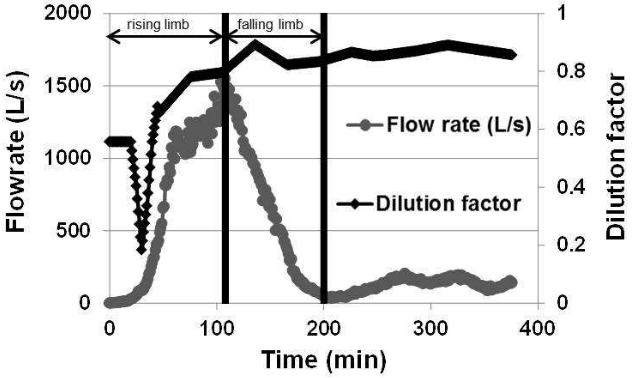
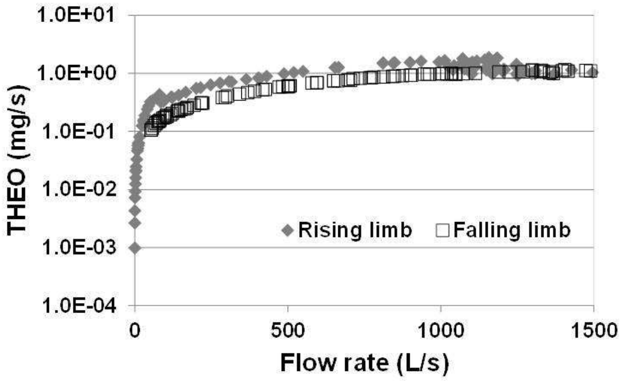
GRAPHICAL ABSTRACT





ABSTRACT

A combined sewer overflow (CSO) outfall was monitored to assess the impact of temporal mass loads on the appropriateness of treatment options. Instantaneous loads (mass/s) varied by approximately three log during events (n=9 in spring, summer and fall) with no significant seasonal variations. Median fraction of total loads discharged with the first 25% of total volume ranged from 28% (theophylline) to 40% (Total Suspended Solids (TSS)) and loads remained high for the duration of the events. *E. coli* and TSS loads originated primarily from wastewater (WW) (63% and 75% respectively). However, a mix of stormwater (SW) and sewer deposit (SD) resuspension contributed from 73 to 95% for the first 50% of the volume discharged of total TSS loads for 2 events. The contribution of SD resuspension was not negligible for Wastewater Micropollutants (WWMPs), especially for carbamazepine. Sustained high loads over the course of CSOs highlight the need to revisit current CSO and SW management strategies that focus on the treatment of early discharge volumes.

KEYWORDS

CSO, sanitary sewers, fecal contamination, *E. coli*, caffeine, carbamazepine, acetaminophen

Introduction

Combined sewer systems (CSS) are generally used to evacuate wastewaters in many of the largest cities in the world; as an example, approximately 40 million people are served by such systems in the United States[1]. During intense rainfall periods, wastewaters and stormwaters are mixed in the combined sewers and the total flow can exceed the transport capacity of the sewer network and/or the treatment capacity of the wastewater treatment plant (WWTP). The excess flows, called combined sewer overflows (CSOs), are generally released directly into the receiving surface waters without any treatment. CSOs have been identified as a major source of microbiological and physico-chemical contaminants (including wastewater micropollutants (WWMPs))[1-7] and are widely known to severely degrade the quality of the receiving natural environments[1, 2, 8]. Acute and cumulative receiving water contamination is a concern because of its impacts on both public health and the economy with regards to bathing area closures, fish and shellfish consumption restriction and drinking water resource contamination[1, 2, 8, 9]

CSO concentration and/or load characterizations are usually performed in environmental studies with regards to classical physico-chemical parameters (Total Suspended Solids (TSS), organic matter, nutrients). Studies examining WWMP compounds and/or microbiological contaminants in addition to physico-chemical characteristics in CSOs are rare and generally rely upon composite sampling[3, 5-7].

The temporal variability of TSS, *E. coli* and WWMP loads is rarely assessed although it is needed for source water protection planning[10] and evaluating potential treatment options[11]. WWMP concentrations in receiving waters, WWTP effluents and CSOs can be used to estimate CSO WWMP loads, especially for components well removed by treatment. WWMP mass balances can be used for a first assessment of the potential contribution of CSOs to trace contaminant loads in receiving waters[12-15].

Concentrations of contaminants during CSO events result from different simultaneous phenomena: (1) the concentration in sanitary waters, (2) internal sewage contribution by in-sewer sediment resuspension and (3) contribution from external stormwater draining to the sewers[16, 17]. Studies have shown the importance of the contribution of sewer deposit (SD) resuspension, which in some circumstances can account for up to 80% of TSS total loads and for up to 71% of *E. coli* total loads during CSO events [3, 16-18]. SDs are known to have a high content of organic matter which is a controlling factor in the retention of pharmaceuticals in soils[19] and thus, SD could be a sink for WWMPs. The high variability of SD resuspension depends on the sewershed, the sewer system configuration, the rainfall intensity and the antecedent dry period. Little is known about the dynamic processes during an event for a combination of *E. coli*, TSS and WWMPs and these data are needed to understand how the system will respond to changes in the sewershed (e.g. implementation of best management practices or treatment processes). The contribution of SD resuspension was shown to impact TSS loads during an entire event and not just at the beginning of a rain event[17]. But, to our knowledge, similar studies have not been performed on microbiological parameters and WWMPs. CSO loads and concentrations also provide an indication of potential concentrations and loads from WWTP effluent in the case of treatment failure. WWTP and CSO waters have been characterized with regards to several hormones and pharmaceutical compounds loads[5]. Although WWMPs and *E. coli* have been investigated with regards to their concentrations[20], their relationships with flowrates and loads need to be elucidated to evaluate CSO management and treatment options.

SD can be considered as a reservoir of microbial contaminants[21] and studies are needed for microbiological parameters as well as human discharge contamination tracers in order to assess public health risk of CSOs.

The main objective of the present study was to investigate the impact of temporal mass loads of *E. coli*, TSS and WWMPs on CSO management strategies.

The specific objectives of this paper were to: (1) assess *E. coli*, TSS and WWMP mass loading variability within and across CSO events for an entire year, (2) estimate seasonal mass loadings of *E. coli*, TSS and WWMPs discharged by a CSO outfall, (3) determine source processes (wastewater, runoff and sewer deposit resuspension) and assess their relative contribution to CSO loadings during events and (4) determine the impacts of contamination sources and their temporal variability on the potential efficacy of management and treatment options.

Materials and Methods

Study site

The studied CSS serves approximately 280,000 residents of the Greater Montreal Area and conveys the sewage to an advanced primary wastewater treatment plant (WWTP) treating approximately 240,000 m^3/d. Treatment consists of screening, grit removal, primary settling and UV disinfection from May to October. The WWTP is the only facility that discharges treated wastewater along the studied portion of the river (approximately 40 km) (Figure 1). Approximately 100 CSO and sanitary sewer overflow outfalls were identified for this sewer system (Figure 1) and some have been characterized with regards to frequency and flowrate. Canadian provincial regulations restrict the annual discharge frequency for each outfall based upon the time of the year, the form of precipitation (rainfall vs snowmelt) and the assimilative capacity of the receiving water. From 2009-2011, 1411 overflow events occurred on average per year[22] for this sewage collection system along the river. A total of 27 of these outfalls are located upstream from Drinking Water Intakes (DWIs) (Figure 1).

Sample collection

CSO events (n=9) as well as WWTP influent (n=13) and effluent (n=12) were monitored between October 2009 and July 2011.

CSO events were sampled during three different seasons (spring (n=2), summer (n=3), fall (n=4)) at one overflow outfall (overflow A – OA) (Figure 1). Grab samples were also collected in the sewershed A (SA) (n=9) in dry weather conditions, immediately upstream of the CSO outfall to assess raw sewage mean concentration and variability and thus, the relative contribution of wastewater to CSO loads. In order to compare loads discharged by both WWTP and CSOs, WWTP effluent was characterized by daily (24h) flow-proportional composite samples, collected in both dry and wet weather conditions, as well as WWTP influent.

CSO sample collection was performed using automated ISCO samplers (Teledyne ISCO, NB, USA) equipped with an ISCO 750 area velocity module (Teledyne ISCO, NB, USA) recording water level and average cross-sectional velocity at a time step of 1 minute as soon as the water level exceeded 10 cm in the conduit. CSO samples were collected every 5 minutes during the first 30 minutes and then each 30 minutes over the course of 6 hours (when events lasted 6 hours or more) (n=138). More information with regards to CSO outfall, sampling methodology, samples conservation and preservation are available elsewhere[20]. *E. coli* concentrations for event 7 were only available for the beginning of the event because of analytical difficulties. Thus, *E. coli* concentrations below the detection limit in event 7 were not included in the interpretation of results requiring the full event data, but were studied with regards to intra-event variations. Only *E. coli* concentrations were analyzed for event 9.

Analytical Methods

E. coli concentrations were measured using the IDEXX Quanti-Tray 2000 method (IDEXX, ME, USA) having a detection limit of 1 MPN/100mL. WWMP selection was explained elsewhere[20] and WWMPs were analyzed by an on-line solid-phase extraction combined with liquid chromatography electrospray tandem mass spectrometry with positive electrospray ionisation (SPE-LC-ESI-MS/MS). The analytical method was previously described in detail[23, 24]. Detection limits were 9 ng/L for caffeine (CAF), 2 ng/L for carbamazepine (CBZ), 6 ng/L for theophylline (THEO) and 10 ng/L for acetaminophen (ACE) (as estimated from 5 replicate measurements of a field sample and corresponding to three times the standard deviation). All samples were analyzed in duplicate and all CSO and raw wastewater samples were above the detection limit. Laboratory and field blanks were analyzed and all values were below detection limits. WWMP uncertainties with regards to analytical methods were expected to be lower than 25%[25]. Total Suspended Solids (TSS) concentrations were analyzed in accordance with Standard Methods[26] and associated uncertainties with regards to analytical methods were expected to be less than 10% [26].

Calculations

Determination of flowrate

Flowrate calculations were estimated at 1 min intervals with the Flowlink software (Teledyne ISCO, NB, USA) to have an average relative uncertainty varying from 4 to 26% depending on the event[27, 28]. Velocity values were not measured for a 160 min period during event 8 due to technical problems. Missing velocity data were interpolated using a polynomial regression calculated from level and velocity measurements recorded before and after the technical issue. Flowrates were then calculated using the area velocity relation[28]. Even if the uncertainty relative to the extrapolation method could not be determined, the source of uncertainty was considered in the interpretation of the results.

Loads and Event Mean Concentrations (EMCs)

The sample collection was initiated when the water level in the overflow pipe exceeded 10 cm as measured by the area-velocity module (Teledyne ISCO, NB, USA) and samples were collected every 5 min for the first 15 min and then every 30 min for the next 6 hours. As flowrate measurements and sample collection did not follow the same interval of time, concentration data were interpolated using Matlab 7.1 (Mathworks, MA, USA) to determine intermediate concentration values between samples. The contaminant concentrations at the beginning of the event (as recorded by the area velocity module) was set to equal the concentration of the first sample collected. As the final sample typically occurred prior to the end of the event, the final concentration was used to represent the concentration until the end of the event, as proposed elsewhere[29]. Loads were calculated for each time interval by multiplying the concentration by the volume. For each event, total loads were calculated and then, EMCs were determined by dividing the total load by the total volume. Uncertainties ranged from 5 to 65% for loads and from 10 to 52% for EMCs. However, we judged worthwhile to only used interpolated concentrations up to the last sample collected to reduce uncertainties. Thus, except for EMCs, figures and data analysis did not take into account concentrations or loads estimated after the last sample collected.

Statistical methods

As CSO load data were neither normally nor log-normally distributed, non-parametric statistical analyses using Spearman's rank correlation and Kruskal Wallis tests were performed in Statistica Version 10 (Statsoft, OK, USA) and differences were considered significant if $p<0.05$, unless otherwise stated. Box-plots show 10th and 90th percentile (box), median values (square in the box) and whiskers corresponding to the minimum and maximum values. Outliers and extremes are represented by circles and asterisks, respectively, and were both determined using an outlier coefficient of 1.5. Analysis of the trends of EMCs to event mean flowrate was performed on log transformed data using linear regression. A covariance analysis was performed to compare the significance of the EMC factor (CSO, WWTPinfluent (WWTPaff) and WWTPeffluent (WWTPeff)) on each of the responses using log Flowrate as a covariate. The covariance analysis results (Figure S1 and Table S1 in the Supplementary Information) show that in all cases the EMC factor has a significant impact on each of the responses. Tobit regression was not warranted[5] as the data were not left censored because of low WWMP detection limits.

Source apportionment model

The loads in overflows (L_{CSO} [X/min]) result from the apportionment of wastewater loads (L_{WW} [X/min]), stormwater loads (L_{SW} [X/min]) as well as loads resulting from sewer deposit resuspension (L_{SD} [X/min]), (where X could be MPN, mg or ng depending on the contaminant) (Equation 1) and were calculated with measures performed during the overflow event (Equation 2). Wastewater loads were calculated (Equation 3) and the sum of runoff and sewer deposits resuspension were estimated with the following mass balance (Equation 4).

$$L_{CSO}(t) = L_{WW}(t) + L_{SW}(t) + L_{SD}(t) \qquad (1)$$

with

$$L_{CSO}(t) = (C_{CSO}(t) \times V_{CSO}(t)) \qquad (2)$$

$$L_{WW}(t) = C_{WW} \times HCR \times Q_{WW} \times QR \qquad (3)$$

$$L_{SW}(t) + L_{SD}(t) = L_{CSO}(t) - L_{WW}(t) \qquad (4)$$

Where C_{CSO} (t) is the concentration measured in CSO samples. $V_{CSO}(t)$ is the volume discharged for each time interval ($V_{CSO}(t)$ (L)= Q_{CSO} (L/s)* 60), C_{WW} [MPN/L, mg/L or ng/L] is the median concentration measured at the sewage outfall in dry weather conditions, HCR is the hourly concentration ratio estimated with the ratio between the concentration measured each hour and the average daily concentration of the WWTP influent [dimensionless], Q_{WW} is the wastewater flow rate observed in the sewer in dry weather conditions and was fixed to be 500 L/s, i.e. 60% of maximal flow rate capacity, based on the design characteristics of the sewer[3], QR is the flow rate ratio as a function of the time of day and accounts for temporal variability of flow and was determined elsewhere[30] [dimensionless].

Our approach differs from the methodology developed in other studies[16-18] as runoff concentrations were not directly measured in the sewershed studied. Therefore, CSO loads apportionment will be presented and discussed as fractions coming from WW and the sum of SW and SD.

Results and Discussion

A representative example of the variations of flowrate and concentrations of *E. coli*, TSS and WWMP concentrations during a CSO event is presented in Figure S2 in the Supplementary Information.

Temporal load variations in CSOs

Within event variations

Examples of flowrate and mass load variations during an overflow event (#7) are presented in Figure 2. *E. coli*, TSS and WWMP loads increased with flowrate and these variation patterns were similar for other events. Two limbs could be identified corresponding to the rising and falling limbs of the flowrate. In general, loads increased rapidly (by approximately 3 log during the first limb), then tapered off before falling during the second limb as the flowrate decreased. Loads measured were always higher for the rising limb than for the falling limb for a given flowrate. For event 7, load average values during the first limb were approximately 2 times higher for CAF, CBZ, ACE and TSS and 24.5 times for *E. coli* than during the falling limb (Figure 2). Ratios between the average loads for both limbs were calculated for three flowrate ranges (100 to 500 L/s, 500 to 1000 L/s and up to 1000 L/s) and differences among ratios were more pronounced at flowrates lower than 1000L/s. The differences were higher at flowrates of 50-500 L/s while smaller differences were noted at flows exceeding 1000 L/s (17.0 to 1.3 times for CAF, approximately 7.5 to 1.5 times for CBZ and ACE and 8.8 to 1.4 times for TSS). *E. coli* loads were available for the rising limb and only for a few samples for the falling limb of the event. The event occurred during the night (from 1 to 7am) and thus, the concentration fell to below the detection limit (as per the usual dilution used during analysis) during the falling limb.

Given the uncertainty of the *E. coli* concentrations in the falling limb, only measured values above the detection limit are presented. The dilution factor increased with the flowrate and remained high even during the limb of decreasing flowrate for event #7.

The high variability of studied contaminant loads during an event results from a combination of the variation of flowrate and concentrations that depend on raw sewage concentrations, the dilution by runoff water, the time of the day[20] and the resuspension of pollutants from SD that are lower during the falling limb. From t=201min to t=378min, flowrate values were low, ranging from 34 to 204 L/s and the volume discharged corresponded to 14% of the total volume. However, during this period of low flow, loads were generally not negligible for WWMPs as cumulative loads were 9% of CAF and CBZ, 18% of ACE and 20% of THEO of the total load discharged. This large variability of load values demonstrates the importance of studying load temporal variations for source water protection, as concentrations of contaminants at drinking water intakes will be determined by the temporal variability of all cumulative loads.

The fraction (%) of total loads discharged with regards to event volume fraction for the 9 events monitored is presented in Figure S3 in the Supplementary Information. Median fraction of total load discharged with the first 25% of total CSO volume varied between 28% (THEO) and 40% (TSS). No significant first flush effect was observed when using the stringent definition of 80% of the total contaminant mass has to be discharged with the first 30% of the volume[11]. Furthermore, the first flush is a rare phenomenon, site-specific, and can be used to develop strategies with regards to the treatment of wet weather flow discharges[31]. In this study, between 72% (THEO) and 87% (TSS) of total loads median values were discharged with the first 75% of the total volume. During the discharge of the final 25% of the total CSO volume, the loads remained high with an average value of 1.7×10^9 MPN/s and15.5 mg/s for *E. coli* and TSS, respectively. Sustained high loads over the course of CSO events have to be considered in CSO and WW management strategies that focus on the treatment of early discharge volumes.

Inter-event variations

When considering all events, median loads were estimated at 1.30×10^9 *E. coli*/s, 0.44 mg CAF/s, 0.01 mg CBZ/s, 0.59 mg ACE/s, 0.31 mg THEO/s and 12.8 g TSS/s. Of note, the instantaneous compound loads varied by approximately three orders of magnitude during each event (Figure S4 in the Supplementary Information).

Overall, no significant seasonal variations of loads were observed among snowmelt, summer and fall sampling events (Figure 3). Median *E. coli* and TSS loads were respectively 2.1×10^9 MPN/s and 15.0 g/s in snowmelt period, 3.5×10^9 MPN/s and 20.4 g/s in summer as well as 1.8×10^8 MPN/s and 9.6 g/s in fall (Figure 3). CSO events occurring during the snowmelt period were 2 times less frequent than events occurring during the summer but were 2.5 times longer[22]. As recreational uses are limited in winter in Canada, federal guidelines generally do not restrict the frequency of CSO discharges and by extend do not require the disinfection of the WWTP effluent during the snowmelt period. According to the common belief, CSO concentrations in snowmelt periods are likely to be highly diluted. However, our data showed elevated concentrations and loads discharged by CSOs during snowmelt that will have a major impact on river water quality. CSO frequency during snowmelt should therefore be regulated and considered in discharge limits as they may constitute a threat to drinking water intakes and other water usages downstream.

Source contribution in CSOs

Identification of apportionment processes

Figure 4 shows daily average concentration in the influent and effluent of the WWTP versus mean daily flow and the EMCs of various CSO events plotted versus their average flowrate.

EMCs of contaminants studied in CSOs expressed as a function of the mean CSO event flowrate showed a slope lower than 1 (in Log-Log plots) (Figure 4). This indicates that when the flowrate increases, the concentrations decrease at a slower rate suggesting an increasing contribution of non-wastewater sources to the loads. This trend was previously observed[5] for hormones and WWMP concentrations in CSOs by using a statistical concentration-discharge model with flowrates ranging from 14 to 3,000L/s. Figure 4 shows three groups with regards to the concentration-discharge slope: TSS (with a slope of -0.13), *E. coli* (with a slope of -0.32) and WWMPs (with slopes ranging from -0.40 to -0.60). All slopes remain above -0.7 and thus, are indicative of significant sewer or external contributions to the CSO[5]. For the range of mean CSO event flowrate investigated, EMCs cannot be explained solely by dilution. TSS concentrations coming from both SD resuspension and suspended solids from stormwater runoff are not negligible. TSS loads in CSOs were previously identified to originate predominantly from SD resuspension and to a lesser extent from runoff[3, 16]. With regards to *E. coli* and WWMPs, internal contributions including sewage are of greater importance than external contributions coming from runoff. *E. coli* concentrations in SW are approximately 2 log lower than in WW[20] and WWMPs should not be found in runoff. CAF EMCs in our CSOs (the only WWMP common to both studies) are lower than CAF concentrations adapted from the study of Phillips et al.[5] (Figure 4C) because concentrations in raw sewage of our study are lower due to a higher per capita water usage and significant infiltration[30].

Temporal variations of source contribution

The source apportionment of CSO water samples was estimated for each event. The resulting estimates of wastewater and the combination of stormwater and sewer deposit contributions (as a percentage of total CSO loads) are presented in Figure 5. Calculations were performed for each portion of 25% of the total volume discharged. Source apportionments were highly variable, especially for *E. coli* and TSS resulting from flow and concentration dynamics observed within events[14] and overall between events.

By observing the median value, approximately 75% of TSS came from WW and 25% from the combination of SW and SD during events (Figure 5 B). However, events 3, 5 and 7 were distinct as TSS loads originated primarily from SW and SD (from 73 to 95%) for the first 50% (events 3 and 5) or for the first 75% (event 7) of the total discharged volume (data not shown). No relationship was observed between the antecedent dry period for these events and the fraction of the total load discharged. However, maximum flowrate values for these 3 events were from 2.4 to 30.8 times higher (Qmax=3485, 2037 and 1549 L/s for events 3, 5 and 7 respectively) than maximum flowrates observed for the other events. The highest load proportions from the sum of SW and SD were always observed with the first 25% of the volume discharged, which coincided with an increase of flowrate. The contribution of TSS in sewer deposit resuspension has been characterized[18] and (1) varied significantly from one rain event to another, and (2) exceeded 60% for high-intensity rain events. Our results showed that loads came predominantly from WW rather than SW and SD during snowmelt events when the mean and peak flowrates were the lowest. *E. coli* loads came primarily from raw sewage (median value of 63%), as mentioned in a previous study[20], and to a higher extent towards the end of CSO events.

E. coli loads originated predominantly from the mix of SW and SD throughout events 3 and 5 and for the first 75% of the discharged volume of event 9. As previously discussed, *E. coli* concentrations in SW runoff are approximately 2 orders of magnitude lower than in wastewaters, thus, the contribution of *E. coli* from runoff is expected to be negligible compared to raw wastewater[3, 20]. Elevated concentrations of *E. coli* in SW have generally been associated with wastewater or septic cross-connections[24, 32]. SD were also previously reported to contribute to approximately 45% of total *E. coli* loads[3] for a CSO event resulting from an intense rainfall. The fate of *E. coli* depends on its build-up and persistence in SD as they are known to have a highly organic layer favourable for the survival of fecal bacteria[3, 21, 32].

WWMPs originate mainly from WW from the beginning to the end of CSO events, as a WW contribution median value of 100% was observed for CAF, ACE and THEO and reached at least 95% for CBZ for the total volume discharged (Figure 5 C, D, E and F). These results are confirmed by the fact that WWMP concentrations in CSOs were found to depend primarily on raw sewage concentrations and the level of dilution[20]. Nevertheless, SD and SW contribution of WWMP was sometimes identified to be significant, especially for events 5 and 7. Generally, the largest fraction of WWMPs was discharged with the first 50% of the total discharged volume and reached 78 % for CAF (event 5), 86% for CBZ (event 3), 56% for ACE (event 7) and 46% for THEO (event 5). Furthermore, as we expected no WWMPs in runoff waters, it can be assumed that the contribution comes exclusively from SDs. SDs were more frequently estimated to be a source of CBZ (5 events of 8 studied) than other WWMPs and that could be explained by the fact that CBZ has a higher Kow value ($\log Kow_{CBZ}$=2.45) and is less biodegradable[19, 24 33].

SDs remain a concern in terms of concentrations released during high CSO flows. More attention has been dedicated to the development of new devices for Real Time Control (RTC) of solids in sewer pipes in order to enable effective management of SDs[34]. Treatment processes of CSO volumes are limited with regards to volumes that can be treated. In this study, the main source of contaminants alternated between raw sewage and SDs and the loads discharged were highly variable during CSO events and remained high until the end. Moreover, a large proportion of the load was not discharged at the beginning of the event, for example with the first 25% of the volume. Thus, the effort to reduce runoff volumes by the application of SW best management practices will reduce CSO volumes but may not sufficiently reduce peak loads as previously shown with the implementation of rain gardens (by allowing SD to increase during dry weather with only a marginal reduction of peak flows for the largest events)[35]. Thus, the cost-to-benefit ratio of such load reduction should be carefully evaluated.

Implications for CSO management

The cumulative impact of all the discharge points (CSO outfalls and WWTP) for a specific period must be considered from an urban drainage management perspective, especially for meeting environmental water quality objectives.

Interestingly, it can be noted on Figure 4 (A, B and D) that daily mean concentrations of TSS, *E. coli* and CBZ decreased in the WWTP influent as flowrate increased. Patterns observed in the WWTP influent are related to the dilution of raw wastewaters with runoff waters which also increase the variability of concentrations between dry and wet weather conditions[36]. However, no specific trend was noted for CAF, THEO and ACE. During high flows, the velocity increases, therefore the travel time in the sewer is reduced. Less biodegradation of the WWMPs occurs when the travel time is reduced. As CBZ is known for its refractory behaviour, dilution is a more important process than biodegradation for this WWMP. In WWTP effluents, TSS and *E. coli* concentrations increased with increasing flowrates (Figure 4A and B). This was previously observed for TSS[5] and *E. coli*[36] reflecting the decrease of the treatment efficiency during wet weather conditions with the decrease of the hydraulic retention time. Furthermore, two sub-groups could be identified for *E. coli* depending on the use or not of UV disinfection at the WWTP (Figure 4A). As expected, *E. coli* concentrations were higher when no UV disinfection was applied. With UV disinfection, *E. coli* concentrations increased with increasing flowrates. As TSS concentrations in the effluent increase with flowrates, one can assume that the fraction of *E. coli* attached to TSS is less efficiently removed in the primary settlers[36] and that the UV efficiency is reduced by the presence of the particles[37, 38]. In our case, no decrease of WWMP EMCs was observed in the WWTP. Our measurements at the influent and effluent of the WWTP indicate that these compounds are not removed by the advanced primary treatment in place (Figure 4C, D, E and F). Thus, their concentrations are influenced primarily by dilution and degradation processes.

The location of CSO outfalls and the duration of events may also cause acute conditions for several subsequent uses such as drinking water treatment located downstream of several of these CSOs[20, 39]. Pathogen loads are critical from a public health perspective and limiting CSO event frequency and duration as well as improving WW treatment are required. Sustained high loads observed over the course of this CSOs study challenge the validity of conventional CSO and SW interception and treatment practices that focus on early volumes to capture a large fraction of the loads. Our observations also demonstrate the need to implement efficient management practices to reduce the volume of CSOs, as capturing the entire volume is generally not technically and financially feasible. Strategies for reducing peak flow in the sewershed could be effective for reducing peak loads, provided that they do not lead to increased accumulation of SDs.

Improving wastewater treatment is essential for the removal of WWMPs and thus, improving aquatic biota protection. However, the upgrade of the treatment at the WWTP will increase the relative contribution of WWMPs from CSOs versus the WWTP. CSO discharges of compounds that are effectively removed during wastewater treatment are known to contribute a substantial portion of the total mass discharged to the receiving water[5, 13]. Contaminant removal efficiency decreases in wet weather conditions at the WWTP resulting in a disproportionate amount of total loads of some contaminants occurring during wet weather, even in the absence of CSOs. Thus, both the treatment of the WWTP and the management of CSOs need to be considered in an urban management plan to improve the quality of water resources.

Conclusions

- *E. coli*, TSS and WWMP instantaneous loads varied generally by approximately three orders of magnitude during each event. Contaminant load variations followed the flowrate dynamics, i.e loadings increased rapidly with flowrate and, then tapered off and falled as the flowrate decreased. Loads were generally higher during the rising limb of the flowrate than during the falling limb.
- Substantial loads are discharged throughout events and not only at the beginning (with the first 25% of the total volume).
- CSO events during the snowmelt period appear to discharge the same range of loads as during other seasons. CSO discharge frequency should be regulated for the snowmelt period as this period has been identified to be critical for downstream drinking water treatment plants.

- *E. coli* and TSS loads appeared to originate primarily from the WW during events even if the contribution of SW and SD resuspension was not negligible. WW was the primarily source of WWMP loads and SD resuspension was not negligible for CBZ loads.
- WWMPs removal requires advanced treatment. Thus, total annual WWMP loads will not be reduced with conventional CSO treatment. RTC and retention of CSO total volumes upstream of DWIs is critical for reducing *E. coli* loads.
- Emphasis should be placed on improving treatment at the WWTP and reducing volumes to be treated in wet weather while considering the reduction of peak loads.

Figure Captions

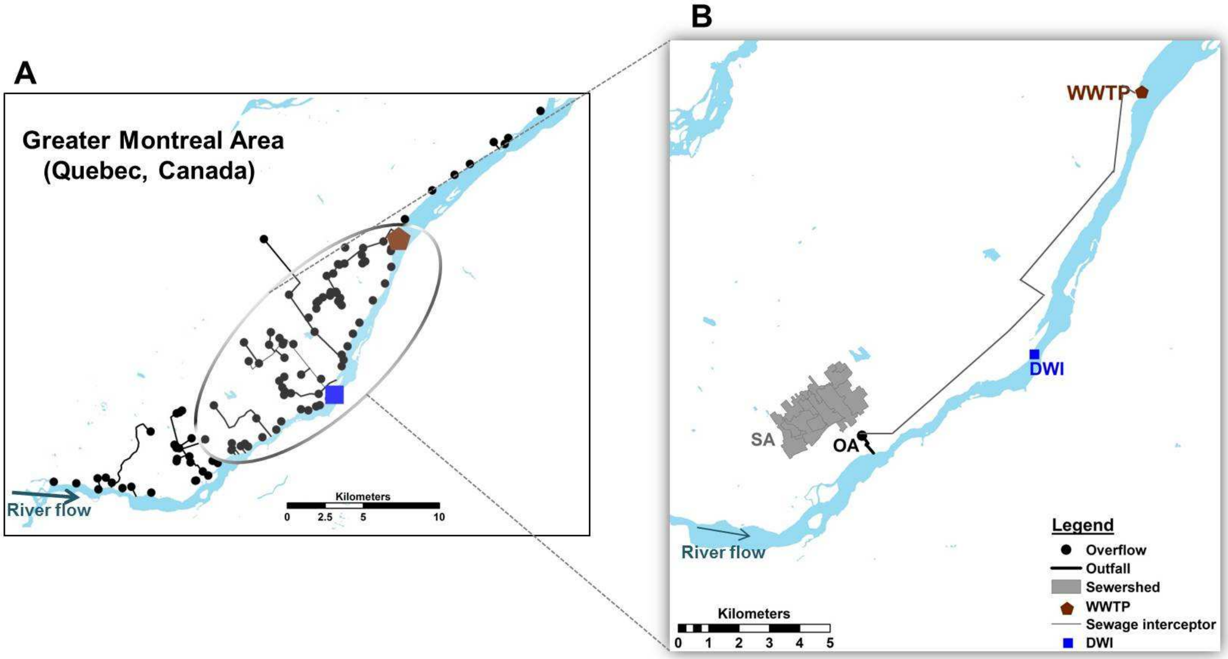
Figure 1: Maps of (A) the study area and (B) the sampling area

[5]Figure 2: (A) Fluctuations of the flowrate and the dilution factor during an overflow event occurring in fall (event 7). Variations of estimated mass fluxes as a function of the flowrate during the flowrate rising limb (grey diamond) (from t=0 to t=108 minutes) and falling limb (empty square) (from t=109 to t=200minutes), (B) *E. coli* (due to analytical difficulties, *E. coli* loads are only represented for some samples for the falling limb), (C) TSS, (D) CBZ, (E) CAF, (F) ACE. The proportion of stormwater, i.e dilution factor, during CSO events was calculated using CBZ as a reference tracer as detailed elsewhere[20].

Figure 3: Box-plots of contaminant loads measured in CSOs for different seasons (SM: Snowmelt (n=713); S: Summer (n=657); F: Fall (n=1022 but $n_{E.\ coli}$=875). (A) *E. coli,* (B) TSS, (C) CAF, (D) CBZ, (E) THEO, (F) ACE.

Figure 4: EMCs of contaminants measured in CSOs (black squares), daily mean concentrations in the influent (circles) and in the effluent (gray diamonds – empty gray diamonds are *E. coli* daily mean concentrations without UV disinfection) of the WWTP versus the mean flowrate in Log-Log plots. (A) *E. coli*, (B) CAF, (C) TSS, (D) CBZ, (E) ACE, (F) THEO. Asterisks denoted significant regression (* for p<0.1 and ** for p<0.05). Black crosses represented the samples published by Phillips et al. [5].

Figure 5 Contributions (%) of wastewater (dark grey) and the mix of runoff and in-sewer deposits (light grey) to CSO contaminant loads as a function of the cumulative fraction of volume discharged. (A) *E. coli*, (B) TSS, (C) CAF, (D) CBZ, (E) ACE, (F) THEO.



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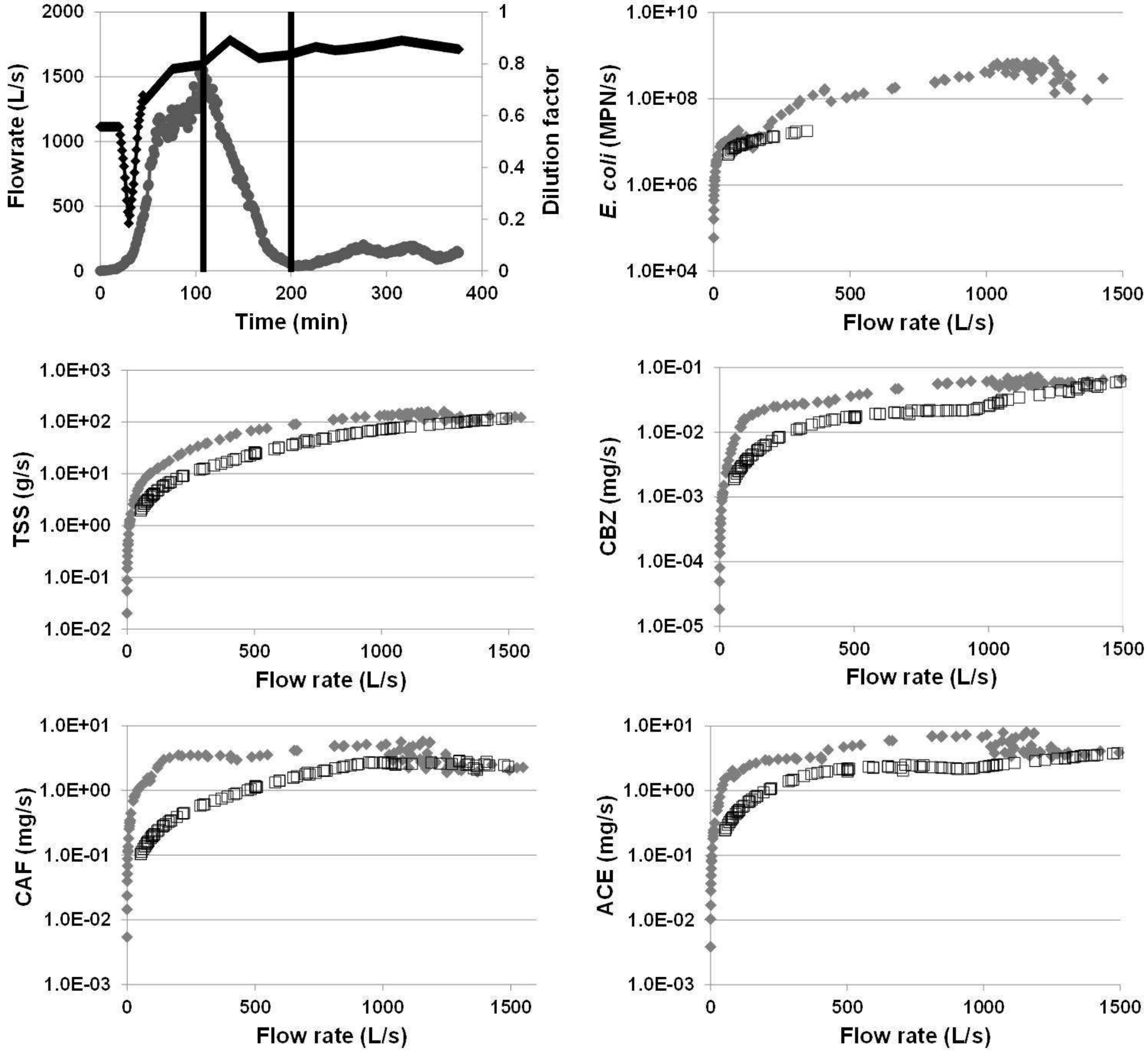

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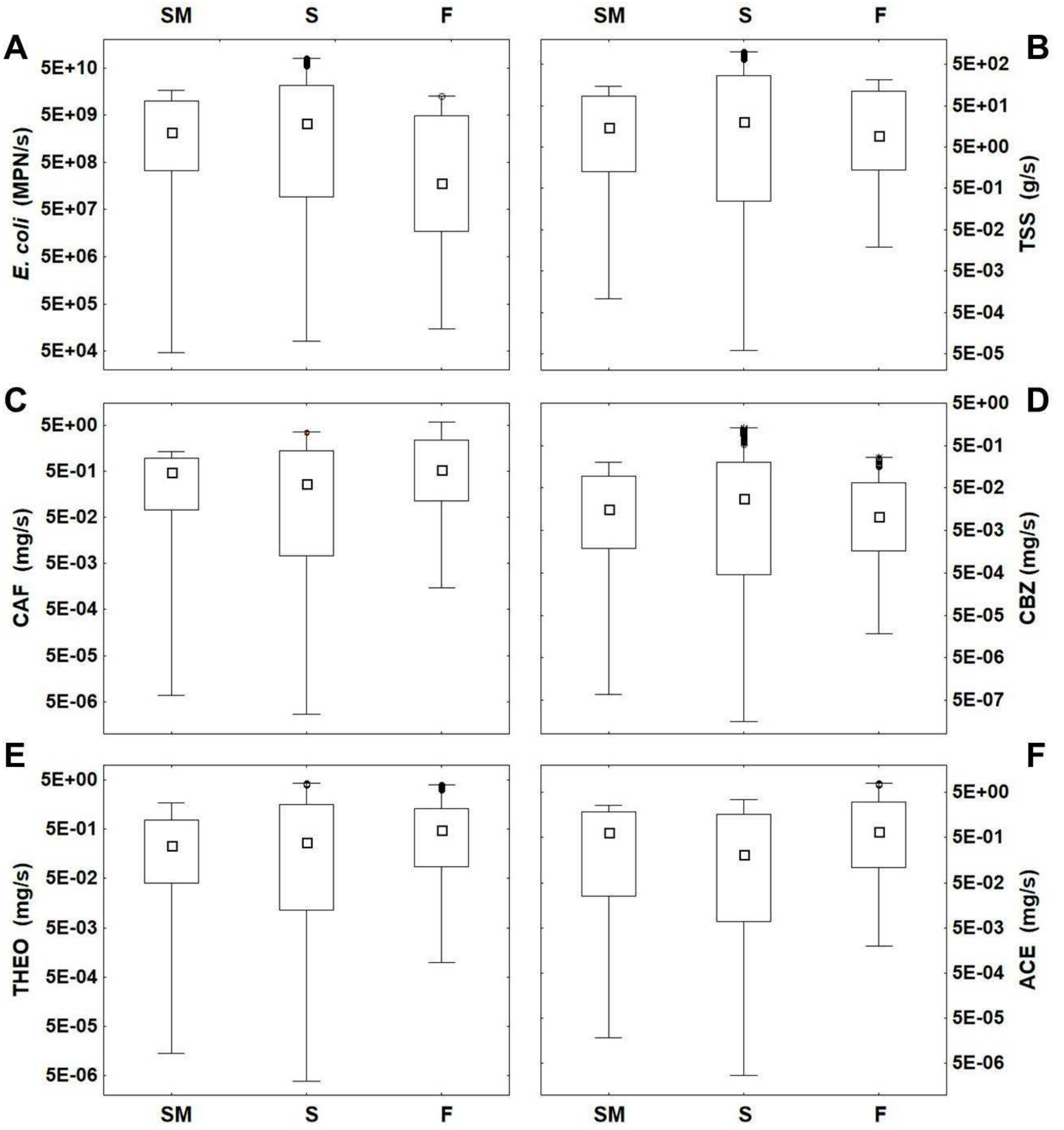
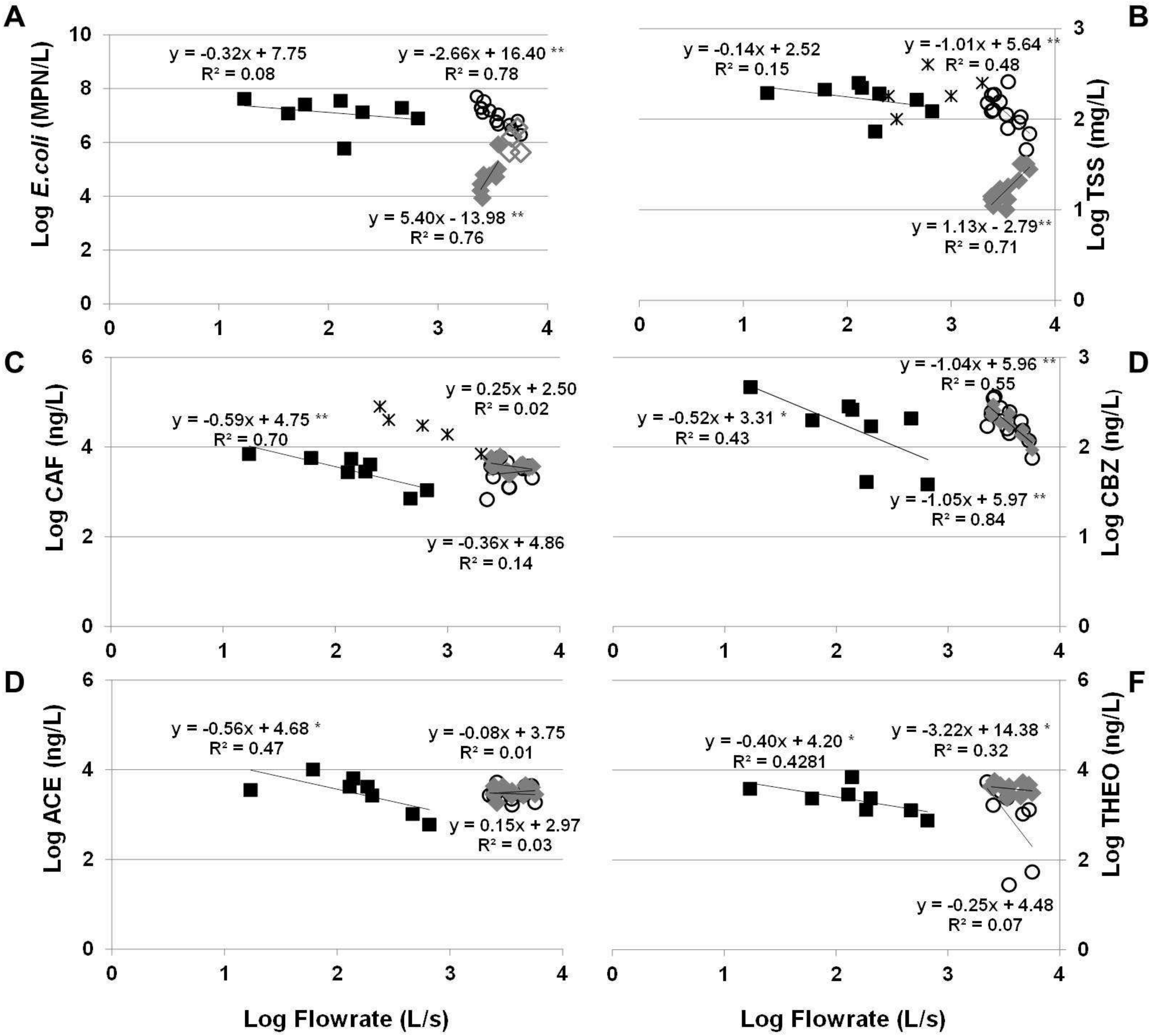


Figure33: Box-plots of contaminant loads measured in CSOs for different seasons (SM: Snowmelt (n=713); S: Summer (n=657); F: Fall (n=1022 but $n_{E.\ coli}$=875). (A) *E. coli,* (B) TSS, (C) CAF, (D) CBZ, (E) THEO, (F) ACE



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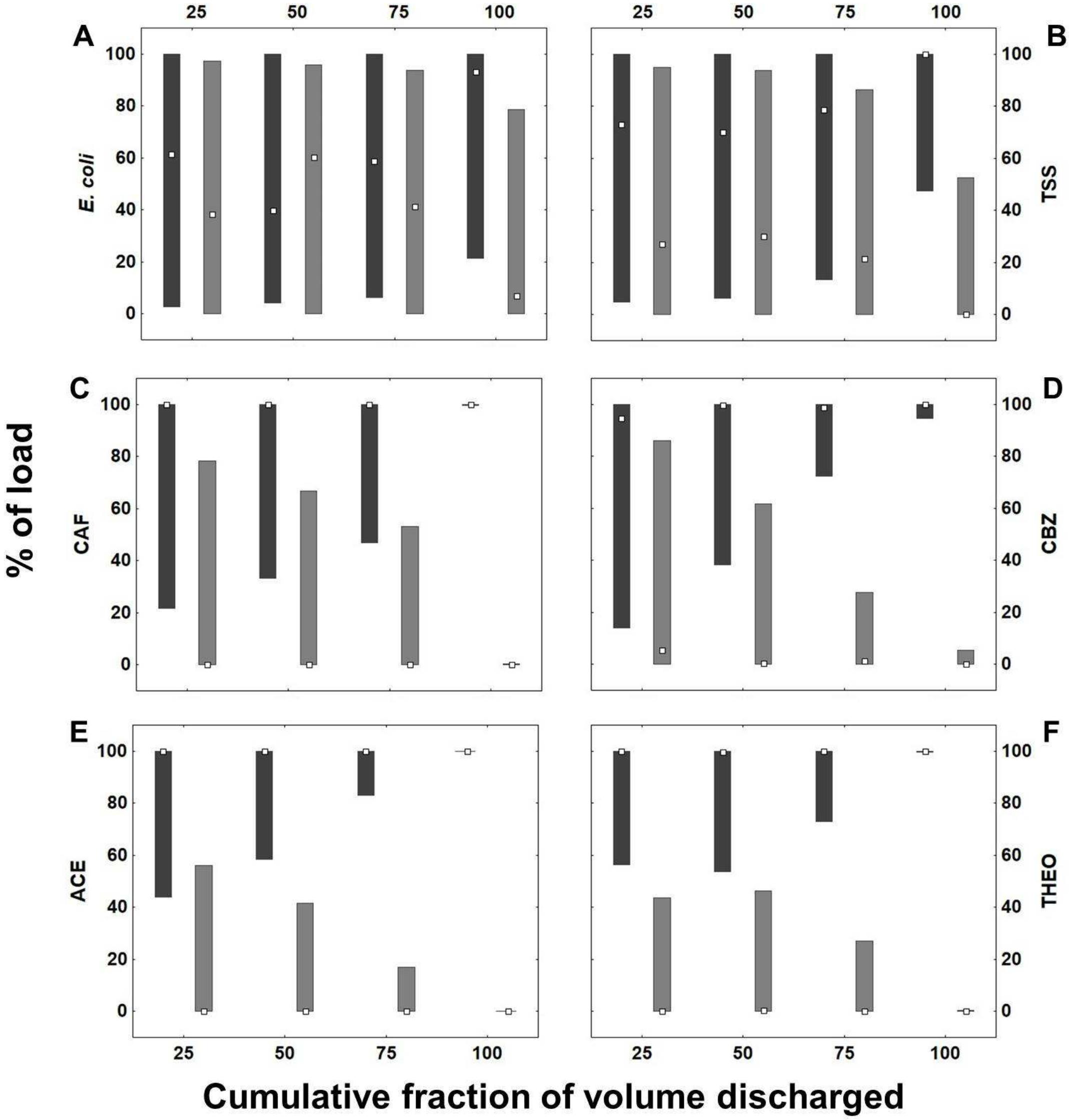

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460 Figure 4: Contributions (%) of wastewater (dark grey) and the mix of runoff and in-sewer

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ASSOCIATED CONTENT

Text that give 4 figures and 1 table is available free of charge via the Internet.

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