Chemosphere 86 (2012) 118–123

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Fecal coliforms, caffeine and carbamazepine in stormwater collection systems in a large urban area

Sébastien Sauvé [a,*], Khadija Aboulfadl [a], Sarah Dorner [b], Pierre Payment [d], Guy Deschamps [c], Michèle Prévost [b]

[a] Département de Chimie, Université de Montréal, Montreal, QC, Canada
[b] NSERC Industrial Chair on Drinking Water, Department of Geological, Mining and Civil Engineering, École Polytechnique de Montréal, Montreal, QC, Canada
[c] Service du Développement et des Opérations, Direction de L'environnement et du Développement Durable, Division de la Planification et du Suivi Environnemental, Réseau de Suivi du Milieu Aquatique, Ville de Montréal, Montreal, QC, Canada
[d] INRS-Institut Armand-Frappier, Institut National de la Recherche Scientifique, Laval, QC, Canada

ARTICLE INFO

Article history:
Received 17 May 2011
Received in revised form 20 September 2011
Accepted 22 September 2011
Available online 8 November 2011

Keywords:
Caffeine
Carbamazepine
Coliforms
Sewer overflows
Sanitary contamination
Chemical indicator

ABSTRACT

Water samples from streams, brooks and storm sewer outfall pipes that collect storm waters across the Island of Montréal were analyzed for caffeine, carbamazepine and fecal coliforms. All samples contained various concentrations of these tracers, indicating a widespread sanitary contamination in urban environments. Fecal coliforms and caffeine levels ranged over several orders of magnitude with a modest correlation between caffeine and fecal coliforms (R^2 value of 0.558). An arbitrary threshold of 400 ng caffeine L^{-1} allows us to identify samples with an elevated fecal contamination, as defined by more than 200 colony-forming units per 100 mL (cfu 100 mL^{-1}) of fecal coliforms. Low caffeine levels were sporadically related to high fecal coliform counts. Lower levels of caffeine and fecal coliforms were observed in the brooks while the larger streams and storm water discharge points contained over ten times more. The carbamazepine data showed little or no apparent correlation to caffeine. These data suggest that this storm water collection system, located in a highly urbanized urban environment, is widely contaminated by domestic sewers as indicated by the ubiquitous presence of fecal contaminants as well as caffeine and carbamazepine. Caffeine concentrations were relatively well correlated to fecal coliforms, and could potentially be used as a chemical indicator of the level of contamination by sanitary sources. The carbamazepine data was not significantly correlated to fecal coliforms and of little use in this dataset.

1. Introduction

Several authors have proposed caffeine (Seiler et al., 1999; Gardinali and Zhao, 2002; Peeler et al., 2006; Wu et al., 2008) or pharmaceuticals products as tracers of human wastes (Seiler et al., 1999; Wu et al., 2008; Kasprzyk-Hordern et al., 2009). Caffeine has the advantage of being ubiquitous and almost entirely human-related, given that there are virtually no agricultural or industrial releases, especially in the Northern hemisphere. Some natural plant sources of caffeine do exist but the background levels thus generated are usually negligible and can thus be disregarded (Peeler et al., 2006). The main sources of caffeine are considered to be coffee, tea, cola, cocoa-containing products and some pharmaceuticals and over the counter medication containing caffeine. The actual contributions from these various sources will vary according to consumption habits. Given that caffeine degrades slowly in the environment with an estimated half-life between 3 d and >3 months – (Benotti and Brownawell, 2009), it has been proposed as a tracer of domestic sanitary contamination.

A large portion of caffeine is metabolized and only about 3% of the ingested molecule is actually excreted through urine (Tang-Liu et al., 1983). Earlier studies have proposed that the contribution from the disposal of unconsumed caffeine-containing beverages and food products may actually be an even greater contributor than actual consumption, given its high metabolism rate, but no actual data were provided to quantify this assertion (Seiler et al., 1999). Concentrations of caffeine have been reported to vary from 20 to 300 μg L^{-1} in raw sewage and 0.1 to 20 μg L^{-1} in treated wastewater effluents (Heberer, 2002; Buerge et al., 2003; Viglino et al., 2007). Reported concentrations in rivers, lakes and seawaters range between 3 and 1500 ng L^{-1} (Buerge et al., 2003) whereas in ground waters values are between 10 and 80 ng L^{-1}. Caffeine has been most studied as a potential tracer of human sewage in surface water including urban/suburban runoff (Standley et al., 2000). Buerge et al. (2003) have shown that caffeine measurements are a direct and sensitive indicator of the presence of wastewater and combined sewer overflow discharges in rivers. Of prime importance when considering using

* Corresponding author. Tel.: +1 514 343 6749; fax: +1 514 343 7586.
E-mail address: sebastien.sauve@umontreal.ca (S. Sauvé).

0045-6535/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2011.09.033

caffeine as a wastewater tracer is the persistence of caffeine in the discharge and receiving waters. Caffeine undergoes slow photochemical oxidation, is not likely amenable to significant sorption or volatilization and the main mechanism for its elimination in lake water is biodegradation (Buerge et al., 2003). Caffeine's half-life has been estimated to range from 3.5 d to more than 100 d in estuarine and coastal waters with lower values observed in trophic waters (Benotti and Brownawell, 2009). Persistence in some surface waters can be astonishingly high. Half-lives in lake water estimated from batch incubations and derived from *in situ* changes of concentrations ranged between 120 and 240 d, while estimated half lives from wastewater biological processes are much shorter (0.8–5 h) (Buerge et al., 2003). However, prior exposure to wastewater discharge can significantly increase the biotransformation rate of caffeine in the water column (Bradley et al., 2007).

Carbamazepine is an anti-seizure drug which is also increasingly used for various psychiatric treatments. Because of its very slow degradation with a half-life estimated to be above 100 d, it has been proposed as an ideal anthropogenic tracer. However, the consumption and usage of this drug will be much lower and less widespread than that of coffee and caffeine-based products, but current analytical procedures can detect ultratrace levels of carbamazepine in surface waters. Reported levels vary between 0.1 and 5 μg carbamazepine L^{-1} in sewage with highly variable removal rates by wastewater treatment plants (WWTP) – with expected concentrations in effluents at similar range (Heberer, 2002; Viglino et al., 2007). Carbamazepine is very slowly biodegraded with half life in estuarine and coastal water exceeding 100 d (Benotti and Brownawell, 2009). Also, carbamazepine is also one of the few compounds which are pretty much unaffected by natural degradation in treatment lagoons (Conkle et al., 2009).

Thermal tolerant coliforms and/or *Escherichia coli* are commonly used to evaluate and regulate the levels of fecal pollution from storm water discharge. Because storm sewers systems collect surface runoff, non-human sources can contribute significantly to fecal indicators such as thermotolerant coliforms and *E. coli*. Storm water discharges can increase the loads of indicators such as *E. coli*. by up to 3–4 log units in receiving waters as compared to background levels measured in dry weather, while median concentrations only increased by about 76% (Aström et al., 2007, 2009) and can contribute significantly to the stream loadings of pathogens such as *Cryptosporidium*, *Giardia* and norovirus (Rechenburg et al., 2006; Aström et al., 2009). More human specific tracers would be extremely useful to establish the sources of contamination and to control them.

Our primary objective was to monitor the levels of a thermotolerant coliforms, caffeine, and carbamazepine in various sections of the storm water collection systems in an urban environment located on the Island of Montréal. The secondary objective was to establish if chemical and microbial indicators could serve as anthropogenic markers in dry weather to assist in identifying potential cross connection in this storm water collection systems.

2. Materials and methods

2.1. Experimental designs

Samples were collected from small streams, brooks, collectors and storm sewer outfall pipes from the storm water system across the Island of Montréal (City of Montreal, QC, Canada) – Fig. 1. The 120 individual samples were collected based on previous surveys so as to: (1) target sites with suspected or confirmed fecal contamination and (2) include a range of fecal coliform densities enabling us to establish whether or not caffeine or carbamazepine could be correlated with thermotolerant coliforms. The samples were collected in June 2008 and October 2008. Samples were taken during wet weather (40) as defined by >15 mm of rain in the 24 h prior to sampling (10/22 – 17 mm, 10/27 – 25&40 mm, 10/28 – 21 mm) and dry weather (80) as defined by <2 mm 24 h prior to sampling (10/05 – 06, 10/20 – 22). All samples were kept at 4 °C and processed for fecal coliforms within 24 h and for caffeine and carbamazepine within 7 d (Aboulfadl et al., 2010) using online solid phase extraction coupled to liquid chromatography and tandem mass spectrometry (SPE-LC–MS/MS).

2.2. Fecal coliforms

Samples were analyzed by the Laboratory of the City of Montreal using Standard Methods 9222 for the detection and enumeration of fecal coliforms on mFC medium by membrane filtration (AWWA, 2005).

2.3. Chemical analysis

We used an automated solid phase extraction coupled to liquid chromatography and tandem mass spectrometry technique (SPE-LC–MS/MS) based on a method for a larger group of compounds which was slightly modified to accelerate the analysis (Viglino et al., 2007). The compounds were identified by retention-time and by their specific SRM transitions at their respective *m*/*z* ratios. The two most intense transitions were selected for each compound: one for the quantification and another for qualitative confirmation. Standard solutions used for quantification were also preconcentrated using the same procedure as the samples. Before each analysis, an internal standard (IS) was added to correct for variations in sample recovery and instrumental performance. Methanol blanks were also injected after every real sample to clean the columns. The peak areas of analytes were normalized to those of the IS. Five specific concentrations ranging from 0 to 100 ng L^{-1}, with a fixed 70 ng L^{-1} of isotope-labeled internal standard, were injected to build up a calibration curve (R^2 values were at least 0.988). Areas of the analytes and IS were calculated by the LCquanTM 2.5 software (Thermo Fisher Scientific). Limits of detection were estimated as three times the standard deviation of 5 replicates measurements of a real sample and were 9 ng L^{-1} for caffeine and 0.2 ng L^{-1} for carbamazepine. Recoveries in real sample ranged from 87% to 110% and blanks were below or close to our detection limits (see {Viglino, 2008} for details).

All samples were analyzed in duplicates. Water blanks (using HPLC water – Baker (Quebec, Canada)) were included every ten samples. The SPE-LC–MS/MS system uses Thermo Fisher EQUan system, including a six-port switching valve to control an analysis consisting in 1.0 mL injection of sample through a 1-mL sample loop at 1 mL min^{-1} onto a preconcentration column (C18, 12-μm, Hypersil GOLD™ column (octadecyl carbon (C18) bounded silica), 20 mm × 2.1 mm i.d) using a Surveyor LC-Pump (Thermo Fisher Scientific). The pre-concentration column is then washed by flushing at 1 mL min^{-1} with a water/formic acid solution at pH 2.6 for 1.4 min. The valve is then switched to use a Surveyor MS Pump Plus (Thermo Fisher Scientific) to back flush the loading column at 200 μL min^{-1} with 0.1% formic acid–methanol (95:5, v/v) directly into the analytical chromatography column (C18, 3-μm Hypersil GOLD™ column, 50 mm × 2.1 mm i.d. – Thermo Fisher Scientific) which is preceded by similar guard column (2 × 2 mm, 5 μm). The chromatography gradients are detailed in Table 1.

A TSQ Quantum Ultra AM Mass Spectrometer (Thermo Fisher Scientific, Waltham, MS, USA) tandem triple quadrupole mass spectrometry fitted with an electrospray ionization source was used for detection. The instrument was operated in positive ionization mode and was directly coupled to the HPLC system at a flow rate 200 μL min^{-1}. Sample analysis was performed in the selective reaction monitoring mode (SRM) – we used for caffeine: SRM 195.0→138.0 with a collision energy of 19 and tube lens of 60