

# Pharmaceuticals in the Yamaska River, Quebec, Canada

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Pharmaceutically active compounds have been detected in North America and Europe in groundwater, surface water, wastewater, and drinking water. In the province of Quebec in Canada, there has been little data to assess the occurrence of pharmaceutical residues in the aquatic environment. In August of 2005, samples of surface water were collected at 10 sites along the Yamaska River basin in Quebec, which passes through important agricultural areas and receives wastewater from several urban centers with populations ranging up to 44,000 residents. Several acidic drugs (naproxen, ibuprofen, gemfibrozil), neutral drugs (caffeine, carbamazepine, cotinine), and the sulfonamide antibiotic sulfamethoxazole were detected in the majority of the surface water samples. The antidepressant fluoxetine (neutral/basic drug) was not detected in any samples, while acetaminophen (acidic drug) was detected at only two sites, and sulfapyridine (sulfonamide antibiotic) was detected at only one site. Sulfamethoxazole and carbamazepine were present at the highest maximum concentrations of 578 ng/L and 106 ng/L, respectively. The concentrations of most of the target pharmaceutically active compounds observed in surface water samples within the watershed were generally consistent with the number of people in urban centers near the sampling sites when compared with other studies in urban watersheds. However, carbamazepine, naproxen, and sulfamethoxazole were present at surprisingly high concentrations for some of the low density areas. Overall, these results demonstrate that pharmaceuticals are distributed in surface waters within a watershed in Quebec at concentrations similar to levels observed in previous studies done in other parts of North America.

**Key words:** pharmaceuticals, surface water, acidic drugs, neutral drugs, sulfonamide

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## Introduction

Pharmaceutically active compounds (PhACs) have been detected in domestic wastewater and in surface water in both Europe (Ternes et al. 1998; Ternes et al. 2001) and North America (Kolpin et al. 2002; Boyd et al. 2003; Metcalfe et al. 2004; Brun et al. 2006). These compounds and their metabolites may have negative impacts on the aquatic environment. The objective of this study was to provide a first reconnaissance of the occurrence of selected PhACs in a watershed in the Canadian province of Quebec. For this study, the Yamaska River basin was selected for monitoring at ten sampling sites. The Yamaska River watershed discharges into the St. Lawrence River at a point approximately 70 km downstream of the city of Montreal. Land use in the region includes agriculture, forestry, and industry. The watershed contains a population of approximately 250,000 people distributed over rural regions and several small to medium sized communities. For this study, sampling sites within the basin were chosen at locations where adjacent populations vary between under 500 to 44,000 people. Inputs of domestic wastewater into the Yamaska River at these sites vary from no direct discharges, to intermittent discharges from sewage lagoons, to continuous discharges from wastewater treatment plants at flow rates up to approximately 50,000 m<sup>3</sup> per day.

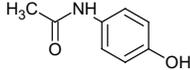
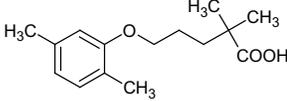
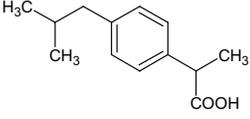
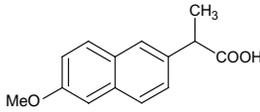
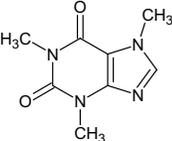
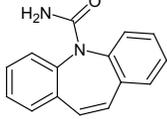
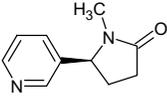
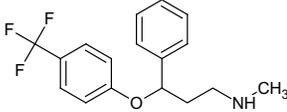
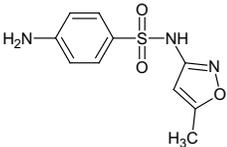
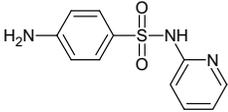
The human-use pharmaceuticals selected for analysis, which are listed in Table 1, were chosen on the

basis of their occurrence in water and wastewater in previous studies in other Canadian provinces (Metcalfe et al. 2004). Target PhACs included 10 compounds from three pharmaceutical classes, including acidic drugs (acetaminophen, naproxen, ibuprofen, gemfibrozil), neutral/basic drugs (caffeine, cotinine, carbamazepine, fluoxetine) and sulfonamide antibiotics (sulfamethoxazole, sulfapyridine). These pharmaceutical compounds can reach detectable concentrations in rivers and lakes if prescription rates are high and the compounds show persistence in the aquatic environment. Although the data collected in this study does not provide information on the fate of the target pharmaceuticals in the Yamaska River, previous studies have shed some light on the processes that influence the behaviour of pharmaceuticals that are released in untreated wastewater. First, the removal of these pharmaceuticals in wastewater treatment plants varies widely. For example, acetaminophen is known to rapidly degrade during secondary treatment (Ternes et al. 1998). Ibuprofen and naproxen are known to also have elevated rates of degradation, while sulfamethoxazole is degraded in wastewater by up to about 60% (Carballa et al. 2004). Carbamazepine is not significantly degraded during wastewater treatment (Ternes 1998; Metcalfe et al. 2003a). Some pharmaceuticals are thus eliminated in wastewater treatment plants, while others largely survive sewage treatment. Partitioning between the aqueous phase and organic biomass (i.e., sludge) in sewage or into sediments can also play a key role in the fate of pharmaceuticals. Since most drugs are relatively water soluble, they occur primarily in the aqueous phase and

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TABLE 1. Target compounds for analysis in water samples from the Yamaska River basin

Name of Analyte	Structure	CAS Number and formula	Use and origin
<i>ACIDIC DRUGS</i>			
Acetaminophen		103-90-2 C <sub>8</sub> H <sub>9</sub> NO <sub>2</sub>	Analgesic and Antipyretic
Gemfibrozil		25812-30-0 C <sub>15</sub> H <sub>22</sub> O <sub>3</sub>	Lipid Regulating Agent
Ibuprofen		15687-27-1 C <sub>13</sub> H <sub>18</sub> O <sub>2</sub>	Analgesic/Anti-inflammatory
Naproxen		22204-53-1 C <sub>14</sub> H <sub>14</sub> O <sub>3</sub>	Analgesic/Anti-inflammatory
<i>NEUTRAL/BASIC DRUGS</i>			
Caffeine		58-08-2 C <sub>8</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>	Stimulant
Carbamazepine		298-46-4 C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O	Anti-Epileptic
Cotinine		486-56-6 C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O	Nicotine Metabolite (in humans)
Fluoxetine		54910-89-3 C <sub>17</sub> H <sub>18</sub> F <sub>3</sub> NO	Antidepressant
<i>SULFONAMIDE ANTIBIOTICS</i>			
Sulfamethoxazole		723-46-6 C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> S	Antibiotic
Sulfapyridine		144-83-2 C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> S	Antibiotic

transfer to sewage sludge or sediments is probably of only minor importance for the majority of compounds (Jones et al. 2005). Machatha and Yalkowsky (2005) reported log octanol-water partition coefficients (i.e.,  $\log K_{ow}$ ) of: caffeine, -0.07; acetaminophen, 0.48; sulfamethoxazole, 0.89; carbamazepine, 2.32; naproxen, 3.26; and ibuprofen, 3.50. Some studies have confirmed that pharmaceuticals such as carbamazepine exhibit low adsorption to solids (Ternes 2001). Photodegradation in the aquatic environment could also play an important role in the persistence of these pharmaceuticals. Based on lab experiments, a wide range of rates of photodegradation of pharmaceuticals have been reported. In addition, the impact of humic materials on photodegradation is significant and differs from one pharmaceutical to another. For example, humic acids act as photoactive filters for carbamazepine and as photosensitizers for sulfamethoxazole (Andreozzi et al. 2003). Data on the half-lives of pharmaceuticals in the environment are very limited in the literature, but the available data indicate a wide range, from 2.4 days for sulfamethoxazole (Andreozzi et al. 2003) to 32 days for ibuprofen and 63 days for carbamazepine (Garric et al. 2005). Finally the continuous release of pharmaceuticals in the environment, from various sources, contributes to the apparent persistence of these pharmaceuticals.

## Methods

### Study Area

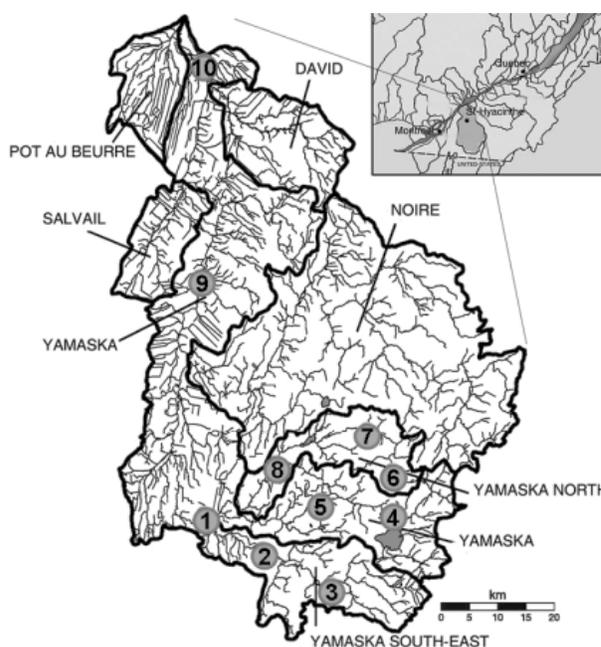
As shown in fig. 1, the Yamaska River is located in the southeastern part of Quebec, approximately 70 km east of the city of Montreal. Its geographical coordinates extend from a point located at the mouth of the river with the coordinates 45°16'0"N, 72°30'0"W to a point at the headwaters with the coordinates 45°18'0"N, 72°35'0"W. The Yamaska River discharges into the St. Lawrence River at the outflow of Lac St-Pierre. The flow rate at that point is of the order of 80 m<sup>3</sup>/s (Primeau and Grimard 1990). The characteristics of the Yamaska River and its watershed have been described in several reports. There is evidence in these reports that land-use activities in the region, including agriculture at 56% of land area, forestry at 37%, urban development at 4.4%, and aquatic ecosystems at 2% (Delisle et al. 1998), have had ecological impacts on the watershed, such as high nitrogen and phosphorus concentrations, presence of pesticides, and growth of cyanobacteria (Tessier et al. 1980; Day et al. 1990; Dutka et al. 1991; Barton and Metcalfe-Smith 1992; Bird 1994; Delisle et al. 1998; Quebec Ministry of the Environment 1985; Desmeules and Gelinas 1977). In 1997, following the implementation of new treatment facilities, the wastewater from 98% of the Yamaska River watershed population was connected to wastewater treatment plants, and 83% of the industries targeted by the provincial Ministry of Environment were conducting wastewater treatment in collaboration

with municipal wastewater treatment plants (Quebec Ministry of the Environment 1999). These industries included agricultural products, metal production, wood processing, chemical processing, and the textile industry.

### Sample Collection

The sites selected for sampling were located along the Yamaska River (sites 1, 4, 5, 9, and 10), the North Yamaska River (sites 6, 7, and 8), and the southeast Yamaska River (sites 2 and 3) downstream of the wastewater discharges for the communities. These sites are identified by numbers from 1 to 10 in fig. 1. Details regarding the urban populations and associated wastewater treatment systems near the ten sampling sites are presented in Table 2. Sites 3, 4, and 6 are located in sparsely populated rural areas which are at the headwaters of the southeast Yamaska River, the Yamaska River, and the North Yamaska River, respectively. Sites 1, 2, 5, 7, and 10 are all located downstream of small communities. Site 8 is located downstream of the most heavily populated community of Granby, and site 9 is located downstream of another heavily populated community of Saint-Hyacinthe.

Grab samples of surface water were collected from the different sites in the Yamaska River watershed. Each sample was collected from shore with a 2-m polyethylene dipper in order to ensure that samples were taken from a well-mixed section. At each site, the sampling pole was rinsed 3 times downstream of the sampling site prior to final collection. Three 1-L volumes of surface water were collected on the 18<sup>th</sup> and 19<sup>th</sup> of August, 2005 at each



**Fig. 1.** Map of the Yamaska River watershed showing sampling sites numbered 1 to 10.

TABLE 2. Information on the population sizes and wastewater treatment systems for municipalities upstream of the sites sampled on the Yamaska River watershed

Site number	Sampling site	Approximate population in 2001 <sup>a</sup>	Wastewater treatment in 2005	Median wastewater flow (m <sup>3</sup> /day) <sup>b</sup>
1	Farnham	8,000	Activated sludge with oxidation step	10,750
2	Cowansville	14,000	Activated sludge with oxidation step	16,800
3	Sutton Junction	2,000	Constructed treatment wetland	23
4	Lac Brome	5,500	Aerated lagoon	4,228 (Intermittent)
5	Bromont	5,000	Aerated lagoon	5,334 (Intermittent)
6	Waterloo	4,000	Aerated lagoon	6,919 (Intermittent)
7	Reservoir Choinière	<500	None	—
8	Granby	44,000	Activated sludge with extended aeration	50,000
9	Saint-Hyacinthe	39,000	Activated sludge	45,000
10	Yamaska	1,700	None	—

<sup>a</sup> Statistics Canada 2001.

<sup>b</sup> Ministère des affaires municipales et régions 2007.

sampling site and placed in individual 1-L amber glass solvent-washed bottles with Teflon lined caps. These samples were prepared for analysis of acidic and neutral/basic drugs, and sulfonamide antibiotics. Unfortunately, the solid-phase extraction procedure normally used for sulfonamide analysis did not work properly for the initial group of samples collected. After optimization of the procedure, it was decided to take an additional group of samples for the analysis of sulfonamide antibiotics. On the 28<sup>th</sup> of August, 2005, 1-L samples of surface water were collected for analysis of sulfonamide antibiotics at sampling sites 1, 8, and 10. All water samples were collected between 10:00 am and 3:00 pm and were transported at 4°C in an electric cooler to McGill University in Montreal (Quebec, Canada). Once delivered to the laboratory, samples were stored at 4°C in a refrigerator and all samples were extracted within two days of collection.

### Sample Preparation and Analysis

The 1-L samples were filtered under vacuum through a 1.0- $\mu$ m Millipore glass-fiber filter (Fisher Scientific, Nepean, Ontario, Canada) that had been prewashed with hexane and acetone. Prior to solid phase extraction (SPE), recovery surrogates were added to each of the samples at a concentration of 10 ng/L. Recovery surrogates included meclofenamic acid for acidic drugs, dihydrocarbamazepine for neutral/basic drugs, and sulfamethizol for sulfonamide antibiotics. These compounds, which were purchased from Sigma/Aldrich (Mississauga, Ontario, Canada), have not been previously detected in water or wastewater in Canada (Metcalf et al. 2004).

The samples were extracted with solid-phase extraction cartridges using three different protocols that have been optimized for acidic drugs and neutral/basic drugs (Metcalf et al. 2003b), and for sulfonamide

antibiotics (Miao et al. 2004). For extraction of acidic drugs, the samples were acidified to a pH of 2.0 by adding 3.5 M H<sub>2</sub>SO<sub>4</sub>. For extraction of neutral drugs, pH was adjusted to 7.5 by adding 1.0 M NaOH, and for extraction of sulfonamide antibiotics, the samples were acidified to a pH of 3.0 by adding 3.5 M H<sub>2</sub>SO<sub>4</sub>. All SPE extractions were carried out with 6-mL Oasis HLB SPE cartridges (Waters Inc., Oakville, Ontario, Canada), and samples were passed through the cartridges at a rate of approximately 20 mL·min<sup>-1</sup>.

After extraction, cartridges were aspirated to dryness, individually wrapped in aluminum foil, and cooled to -20°C. SPE cartridges were placed in a cooler with ice packs and sent to Trent University (Peterborough, Ontario, Canada) where the analytes were eluted from the SPE cartridges according to previously published methods (Metcalf et al. 2003b; Miao et al. 2004). For neutral drugs, the cartridges were eluted three times with 3 mL of methanol. For acidic drugs, the cartridges were eluted two times with 3 mL of 2% ammonium hydroxide in methanol, followed by 3 mL of methanol. For sulfonamide antibiotics, the cartridges were eluted twice with 3 mL of methanol, followed by 3 mL of 2% ammonium hydroxide in methanol.

The eluates were collected in a 10 mL collection tube and concentrated to 0.2 mL. The volume of the samples was made up in methanol to a final volume of 0.2 mL, except for analysis of sulfamethoxazole and carbamazepine, where samples were made up to a final volume of 1 mL. The samples were diluted for the latter two analytes in order to ensure that the concentrations in the samples were within the range of the external standards.

Prior to analysis, the sample extracts were spiked with stable isotope surrogates at a concentration of 10 ng/mL to compensate for signal suppression due to the sample matrix. All deuterated surrogates, except carbamazepine-D10, were obtained from C-D-N Isotopes

(Pointe Claire, Quebec, Canada). Carbamazepine-D10 and all  $^{13}\text{C}$  surrogates were purchased from Cambridge Isotopes (Amersham, Massachusetts, U.S.A). For analysis of acidic drugs, ibuprofen (propionic)  $^{13}\text{C}_3$ , gemfibrozil-D6, acetaminophen-D3, and naproxen- $^{13}\text{C}_1\text{D}_3$  were added as surrogates. For the neutral/basic drugs, caffeine- $^{13}\text{C}_3$ , cotinine-D3, carbamazepine-D10, and fluoxetine-D5 were added as surrogates. For the sulfonamide antibiotics, sulfamethoxazole- $^{13}\text{C}_6$  and sulfamethazine- $^{13}\text{C}_6$  were added as surrogates.

All samples were analyzed for the pharmaceuticals listed in Table 2 by liquid chromatography with tandem mass spectrometry (LC-MS/MS) using methods previously described by Metcalfe et al. (2003b) for acidic and neutral/basic drugs, and by Miao et al. (2004) for sulfonamide antibiotics. Briefly, the acidic pharmaceuticals were analyzed using a Micromass Quattro LC triple-quadrupole mass spectrometer (Manchester, U.K.) with an electrospray interface (LC-ESI-MS/MS). The target compounds were analyzed in negative ion mode. Multiple reaction monitoring with unit resolution on both the first and second analyzer was selected for data acquisition. The neutral drugs and sulfonamide antibiotics were analyzed with an Agilent 1100 series high-performance liquid chromatograph coupled with an MDS Sciex QTrap mass spectrometer (Toronto, Canada) equipped with an atmospheric pressure chemical ionization source (LC-APCI-MS/MS). Multiple reaction monitoring with unit resolution on both the first and second analyzer was selected for data acquisition in positive-ion mode. The ion transitions monitored by multiple reaction monitoring analysis of the pharmaceutical analytes, which are listed in Table 3, are the same as the ones previously reported by Metcalfe et al. (2003b) and Miao et al. (2004).

For quantification, external standards were prepared with different concentrations of the analytes, and fixed concentrations (50 ng/mL) of all surrogates were prepared as internal standards. A linear calibration curve was developed for each class of drug, and the data were adjusted for any signal suppression detected by analysis of the surrogates. Concentrations were further adjusted according to recoveries of the recovery standards (10 ng/L). The recoveries ranged from 73 to 82%, with an average of 77% (standard deviation = 14%). The limits of quantification for each target analyte are listed in Table 4. The limits of quantification were estimated as the amount of analyte that produced a signal-to-noise ratio of 10:1 in samples (1 L) of surface water collected from the Otonabee River (Ontario, Canada) that were spiked with a range of analyte concentrations.

## Results and Discussion

The results of the analysis of samples collected in the Yamaska River basin for acidic drugs, basic/neutral drugs, and sulfonamide antibiotics are summarized in Table 4. Of the 10 target analytes, 7 pharmaceuticals were detected in the majority of the water samples.

TABLE 3: Ion transitions for MRM used for the LC-MS/MS-MRM analysis of pharmaceuticals and stable isotope surrogates<sup>a</sup>

Compound	MRM Transition
<i>ACIDIC DRUGS</i>	
Acetaminophen	152 > 110
Gemfibrozil	249 > 121
Ibuprofen	205 > 161
Naproxen	229 > 170
Acetaminophen-D3	155 > 111
Gemfibrozil-D6	255 > 121
Ibuprofen (propionic)- $^{13}\text{C}_3$	207 > 163
Naproxen- $^{13}\text{C}_1\text{D}_3$	233 > 174
<i>NEUTRAL/BASIC DRUGS</i>	
Caffeine	195 > 138
Carbamazepine	237 > 194
Cotinine	177 > 80
Fluoxetine	310 > 148
Caffeine- $^{13}\text{C}_3$	198 > 140
Carbamazepine-D10	247 > 204
Cotinine-D3	180 > 80
Fluoxetine-D5	315 > 44
<i>SULFONAMIDE ANTIBIOTICS</i>	
Sulfamethoxazole	254 > 156
Sulfapyridine	250 > 156
Sulfamethoxazole- $^{13}\text{C}_6$	260 > 162
Sulfamethazine- $^{13}\text{C}_6$	285 > 186

<sup>a</sup>MRM = multiple reaction monitoring.

Fluoxetine was not detected in any water samples, and acetaminophen was only detected at two locations. The antibiotic sulfapyridine was detected at only one of three sites monitored. The concentrations of the drugs in the Yamaska River are consistent with concentrations reported in surface waters elsewhere in Canada (Boyd et al. 2003; Metcalfe et al. 2003b; Brun et al. 2006; Hua et al. 2006), as well as the concentrations in surface waters in the U.S.A. (Kolpin et al. 2002; Kolpin et al. 2004) and in Europe (Ternes et al. 1998; Ternes et al. 2001; Heberer 2002). As has been noted earlier for pharmaceuticals analyzed in environmental matrices by LC-MS/MS (Miao and Metcalfe 2007), the surface water matrix caused suppression of the signal for all analytes. Therefore, the signals for stable isotope surrogates spiked into the samples were used to accurately quantify the concentrations of pharmaceuticals in the surface water samples.

Ibuprofen, a common anti-inflammatory drug sold without prescription, was not detected in samples from sites near the headwaters of the watershed (sites 1 to 5), but this drug was detected at nanograms per litre concentrations at sites 8 and 9 near the more populated areas of Granby and St-Hyacinthe (Table 4). Similar results were observed for gemfibrozil and naproxen, with the highest concentrations observed in samples collected from the more populated areas of Cowansville, Granby, and St-Hyacinthe. However, these drugs were also detected in water near the less populated locations

TABLE 4. Concentrations of pharmaceuticals in grab samples of surface water (ng/L) collected at 10 sites in the Yamaska River basin, Quebec, Canada <sup>a</sup>

Sampling site	Compounds <sup>b</sup>									
	Acetaminophen (1 ng/L)	Gemfibrozil (1 ng/L)	Ibuprofen (1 ng/L)	Naproxen (2 ng/L)	CBZ <sup>c</sup> (2 ng/L)	Caffeine (5 ng/L)	Cotinine (2 ng/L)	Fluoxetine (2 ng/L)	Sulfamethoxazole (5 ng/L)	Sulfapyridine (0.5 ng/L)
1 Farnham	ND <sup>d</sup>	1.4	ND	3.3	48	9.1	4.2	ND	21	ND
2 Cowansville	3.3	12.0	ND	30.7	77	ND	ND	ND	NA <sup>e</sup>	NA <sup>e</sup>
3 Sutton Junction	ND	ND	ND	ND	106	ND	ND	ND	NA	NA
4 Lac Brome	ND	ND	ND	ND	56	ND	ND	ND	NA	NA
5 Bromont	ND	4.4	ND	ND	28	10.7	ND	ND	NA	NA
6 Waterloo	ND	1.1	1.5	ND	32	9.0	3.5	ND	NA	NA
7 Reservoir Choiniere	ND	2.0	1.7	ND	7	34.7	9.0	ND	NA	NA
8 Granby	ND	6.6	7.1	79.1	67	11.5	4.1	ND	578	0.5
9 St-Hyacinthe	1.0	9.9	20.4	26.3	17	11.1	6.7	ND	NA	NA
10 Yamaska	ND	1.1	1.3	2.1	34	22.5	11.8	ND	50	ND

<sup>a</sup> All samples were collected on August 18-19, 2005, except for samples analyzed for sulfonamide antibiotics, which were collected on August 28, 2005.

<sup>b</sup> Limits of detection identified in parenthesis under each compound heading.

<sup>c</sup> CBZ = Carbamazepine.

<sup>d</sup> ND = not detected.

<sup>e</sup> NA = not analyzed.

of sites 1 and 2 (Table 4). The concentrations observed were slightly lower than the range of concentrations observed by Metcalfe et al. (2003b) in surface water samples collected during a survey in 2000 in the Detroit River (Ontario, Canada) and in Hamilton Harbour (Ontario, Canada): that is, 64 to 141 ng/L for ibuprofen, 12 to 66 ng/L for gemfibrozil, and 94 to 207 ng/L for naproxen. Acetaminophen was only detected at levels above detection limits at sites 2 and 9 (Table 4).

Among the neutral/basic drugs analyzed (Table 4), carbamazepine was present at all sites at concentrations ranging from 7 to 106 ng/L, which is again similar to the range of concentrations observed in the Detroit River and Hamilton Harbour by Metcalfe et al. (2003b): 20 to 185 ng/L. This may reflect the persistence of this compound in the environment as reported by Andreozzi et al. (2002) and Miao et al. (2005). Caffeine and cotinine were detected at concentrations between 4 and 35 ng/L, and there appeared to be a trend to higher concentrations at sites near urban centers with greater populations. The widely prescribed antidepressant fluoxetine was not detected in any of the samples. Fluoxetine has been previously detected at low concentrations (i.e., < 20 ng/L) in surface waters in North America by Metcalfe et al. (2003b), Kolpin et al. (2002) and Boyd et al. (2003).

The concentrations of sulfamethoxazole, an antibiotic widely used for the treatment of urinary and respiratory infections in humans and for various veterinary applications, were much higher than the concentrations of sulfapyridine (Table 4). Concentrations of sulfamethoxazole as high as 578 ng/L were detected in the Yamaska River at a site near the most populated area, Granby. Although this concentration is high, Kolpin et al. (2002) reported a maximum concentration of 1,900 ng/L of sulfamethoxazole in a survey of surface waters in the U.S.A. Sulfapyridine was only detected at the Granby site at a concentration just at the limit of detection (0.5 ng/L).

From these data, it appears that the concentrations of target PhACs in surface waters might reflect inputs from discharges of wastewater from urban centres. However, leakage from septic systems in rural areas cannot be ruled out as a possible minor source. Receiving water flow rates near sampling sites should be taken into account to verify any possible correlation with population density. There was also no evidence of a cumulative increase in the concentrations with distance downstream in the basin. However, the sulfamethoxazole and carbamazepine were detected in all samples at relatively high concentrations. The higher concentrations observed for these two pharmaceuticals may be explained by their lower rates of removal during wastewater treatment, their low degree of partitioning onto solids, and their longer half-lives, as reviewed earlier.

Previous studies reporting indices of nitrogen, phosphorus, and pesticide contamination in the Yamaska River indicated temporal profiles of lower concentrations during the winter (sometimes lower than

limits of detection), increases in concentrations starting at the end of May, a significant increase in June, various spikes in concentration during the summer, and finally, a slow decline starting in the fall (Delisle et al. 1998). Considering that there is also a probable temporal and spatial heterogeneity in the distribution of PhACs, further analysis should be done to study these variations and identify the main factors influencing the concentrations of PhACs in the basin. For example, Kolpin et al. (2004) found that the concentrations of pharmaceuticals in rivers downstream of towns and cities in Iowa, U.S.A. varied considerably with the hydrological conditions, with the lowest concentrations detected during periods of high water flow. The usage patterns for prescription and nonprescription drugs may also vary throughout the year (Heberer 2002; Ashton et al. 2004), contributing to variability in the concentrations of PhACs within the river. Finally, Vieno et al. (2005) reported that PhACs were carried longer distances downstream in a boreal river system during the winter months when snow and ice cover were greatest. Future research in the Yamaska River watershed should thus include an evaluation of both temporal and spatial changes in the distribution of PhACs.

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