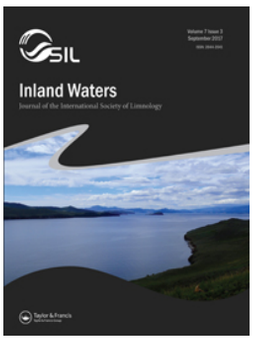

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Trace organic compounds in rivers, streams, and wastewater in southeastern Alberta, Canada

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ABSTRACT

We selected 14 anthropogenic organic compounds representing major classes of potential contaminants for analysis to determine their occurrence in the South Saskatchewan River and its tributaries near irrigated farmland and the only urban center in southeast Alberta, Canada. Agriculture and urban runoff and discharges seem to have little impact on the quality of surface water based on samples taken above and below Medicine Hat/Redcliff in the South Saskatchewan River and local tributaries. Samples of river water, tributary water, and raw and treated wastewater taken over a period of 3 years allowed an estimation of the impact of trace organic compounds from urban and agricultural activities on water quality. Of the 14 compounds investigated, 10 were detected in concentrations above the detection limit in at least one surface water sample and 9 at concentrations above the detection limit in sewage samples. The wastewater treatment plant removed indicator compounds to varying degrees, and the volume of treated effluent discharge was <1% of the river, even during the lowest flow conditions, thereby minimizing potential impact. Discharge in the river and tributaries varied by an order of magnitude over the period of study, including 2 major flood events in the South Saskatchewan River. Potential health or environmental effects were difficult to evaluate from a regulatory perspective because few guidelines are available for reference.

KEYWORDS

Antibiotic; endocrine disruptor; herbicide; industrial chemicals; pharmaceuticals; wastewater; water

Introduction

Pharmaceutical products, endocrine disrupting compounds, and chemicals used in agriculture and industry have been widely detected in various waters worldwide (Sosiak and Hebben 2005). Thousands of anthropogenic chemicals find their way into surface waters, largely secondary to human activities (Snyder et al. 2008), but few are regulated or monitored. These activities include municipal wastewater treatment plant (WWTP) effluent, industrial manufacturing processes, animal feeding operations, and current prescription practices (Snyder et al. 2008). Soluble compounds are subject to modification and degradation by both biotic and abiotic processes, and hydrophobic compounds tend to associate with particulate matter where they may remain suspended or become incorporated with sediments (Anderson et al. 2012). Aquatic organisms are subject to both processes, as are human and animal consumers. By mimicking endogenous hormones, endocrine disrupting compounds may alter development, reproduction, and neural and immune functions (NIH, HHS 2010). This effect is well established in wildlife (Lambert and Skelly 2016).

Monitoring of chemical presence is limited by the high cost of analysis, the need for large sample volumes with extensive processing, and the absence of water quality guidelines for many chemicals, even if they have known toxicity or other harmful effects. Because of the great need for more efficient analytical methods to identify and monitor chemical inputs into rivers and streams, an inexpensive screening tool would be invaluable, and monitoring a select number of indicator compounds is a cost and time effective option (Wunderlin et al. 2014). One option is the enzyme-linked immunosorbent assay (ELISA), which offers faster sample preparation, requires smaller sample volumes with less sample preparation, often has lower detection limits, and is cost effective (Dohnal et al. 2013, Fauzan et al. 2016). The objective of this study was to use ELISA-based kits as a screening tool to estimate the occurrence of representative anthropomorphic compounds in surface waters influenced by

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Supplemental data for this article can be accessed here.

urban and agricultural runoff. The City of Medicine Hat, Alberta, is the only significant source of wastewater discharge in the study area, so raw and treated sewage effluents were included. Here, water resources are scarce, stream inputs are few and seasonal, and multiple upstream agricultural, industrial, and municipal users may influence water quality.

Study site

The vicinity of Medicine Hat is downstream of extensive irrigated farmland and ranching operations, and there is only one major river (the South Saskatchewan) and 2 small streams. The South Saskatchewan River is formed by the confluence of the Bow and Oldman rivers about 75 km northwest of Medicine Hat. Calgary (about 300 km northwest) and Lethbridge (about 120 km west) are the only major centers upstream of Medicine Hat, and there is a large agricultural area irrigated by the Saint Mary River Irrigation District immediately to the southwest of the city (upstream). The Eastern Irrigation District on the north side of the Bow River services the agricultural area surrounding the City of Brooks. Although some potential exists for irrigation return water to reach the river(s) during the growing season, most irrigators use low pressure drop head technology that minimizes wastage (Alberta Government 2014), and runoff potential is low, aided by low precipitation and high evapotranspiration (AMEC 2009). Snowmelt runoff from agricultural areas has the potential to transport contaminants, dependant on prairie spring snow cover. Oil and gas development in the region is extensive, but little is located near watercourses, and its water consumption is only a small fraction of that consumed by agriculture (about 1%; AMEC 2009).

The City of Medicine Hat uses the river for municipal water withdrawals, as does the adjacent Town of Redcliff, constituting about 14% of water use but about 75% of flow returns to the river after extensive wastewater treatment, storm runoff, or groundwater infiltration (data from AMEC 2009). Medicine Hat treats its own raw sewage and that of the Town of Redcliff in the same facility, initially by skimming and settling. The Medicine Hat Wastewater Treatment Plant process starts at the headworks where screens and grit removal chambers remove large objects and larger inorganic material. From there the effluent moves into the primary clarifiers where settling and skimming occur. Chemically enhanced primary treatment occurs at both the headworks and primary locations to coagulate solids in the effluent for easier removal. The floating material skimmed off is removed and taken to the landfill. The settled sludge goes to the sludge thickener, then secondary dewatering, then to the landfill. The effluent from the primary clarifiers proceeds to the trickling filters where aerobic bacteria remove soluble and suspended nutrients as well as some nitrogen. From the trickling filters the effluent goes into the solids contact channels where more flocculation occurs and aluminum sulphate is added to aid in phosphorus removal. Next, the effluent flows into the secondary clarifiers where settling and skimming occur similar to the primary clarifiers. After the secondary clarifiers, the effluent undergoes ultraviolet (UV) disinfection treatment (about 30 mJ/cm^2) and then flows through the lagoon system before being discharged by diffusers into the South Saskatchewan River. The WWTP can handle up to 30 ML/day, which is typically <1% of the discharge in the river, even at the lowest seasonal discharge volumes.

River and creek discharge

Only 2 tributaries, Seven Persons and Ross creeks, flow to the South Saskatchewan River in the Medicine Hat area. They join just before flowing into the river and after flowing through Medicine Hat (Fig. 1). Each tributary receives smaller tributaries that tend to be ephemeral in their headwaters, including Bullshead Creek. In the local tributaries, runoff will typically peak in the spring sometime between April and June, depending on the melting snowpack or the later rainfall events in the headwaters. Creek flows in subsequent months comprise mainly irrigation water releases in the Seven Persons Creek and base flows from groundwater sources in the Ross Creek. High water in the South Saskatchewan River occurs in June each year, originating as snowmelt from the mountains 300 km to the west. In both 2013 and 2014, persistent rainstorms in the headwaters of the Bow and Oldman rivers quickly melted large amounts of alpine snow, augmenting normal river flow and resulting in 100+ year flood conditions downstream. In 2013, discharge in the South Saskatchewan River increased from about 600 m^3/s to more than 5000 m^3/s during 3 weeks in June. This event happened again in 2014, with flows increasing from 300 m^3/s to more than 3000 m^3/s in the latter part of June. The floods were really pulses of water that came and went over a period of a few days and only affected the South Saskatchewan River. They did not result in any substantial increase in local runoff because all of the precipitation fell far to the west, but water backed up in the lowest reaches of Seven Persons and Ross creeks in urban areas, including all downstream sampling sites. Extensive flushing, scouring, and recharge of riparian areas took place along the river's entire length, including industrial, municipal, and agricultural areas. The WWTP remained above water, but there was substantial flooding in the urban areas of Medicine Hat and adjacent agricultural bottomland.

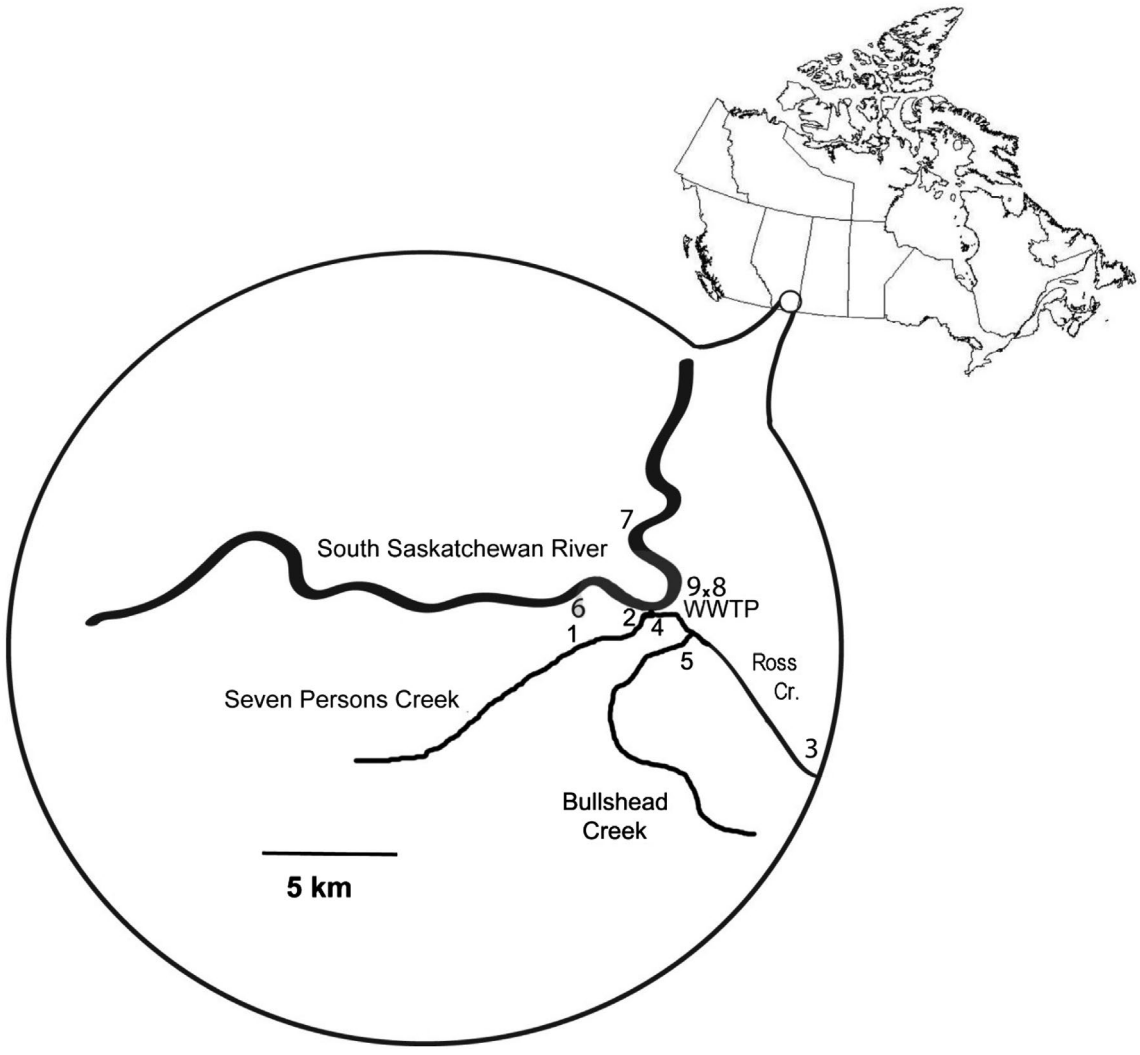

Figure 1. Study area location in Alberta, Canada, identifying the South Saskatchewan River and Seven Persons, Bullshead, and Ross creeks. Numbers 1–7 specify locations of sample sites.

Choice of compounds to investigate

We selected chemicals commonly found in agricultural, industrial, or municipal effluent to represent important classes of contaminants such as human antibiotics or hormones (Table 1). The rationale behind these choices was that these potential contaminants could represent major classes of compounds. Industrial source chemicals were represented by alkylphenol, benzo(a)pyrene, and polybrominated diphenyl ether (PBDE). Avermectins, sulfamethazine, and sulfamethoxazole are widely used human and animal antibiotics, and triclosan is a common antimicrobial compound added to soap and other personal care products. Hormones were represented by estrogen, ethinylestradiol, and testosterone and herbicides by 2,4-dichlorophenoxyacetic acid (2,4-D) and glyphosate. Microcystin is an algal toxin dangerous to livestock and can cause taste and odor issues in drinking water. Caffeine was included as a marker of human sewage.

Methods

Sampling

Sampling occurred approximately twice per month at 9 sites in and around Medicine Hat (Table 2, Fig. 1) during 3 consecutive summers. Sampling also took place in late December 2012 and again in 2013 to capture winter low-flow conditions. The upstream and downstream sampling sites chosen on Seven Persons and Ross creeks and on the South Saskatchewan River were approximately 5 km apart and bracket the region of potential municipal influence. Bullshead Creek drains an upland region of cattle ranching, and the headwaters drain the slopes on the west side of Cypress Hills Provincial Park. Samples were taken using amber bottles with Teflon caps after rinsing the dipper and bottles 3 times with source water and then stored at 2–6 °C. Particulate matter was given time to settle for at least 1 h (samples were not filtered). Analysis began on

Table 1. List of contaminants analyzed in this study and a brief, general description of each.

Contaminant	Description
Alkylphenol	A class of organic compounds; nonylphenol ethoxylates are potent endocrine disrupting compounds used as a surfactant, pesticide ingredient, lubricating oil additive, and for curing of epoxy resins, etc. (Sosiak and Hebben 2005)
Avermectins	A class of macrocyclic lactones extremely active against helminths and arthropods; ivermectin treats parasitic infections in humans and animals; abamectin is used for crop protection (Chung et al. 1999)
Benzo(a)pyrene	An important polycyclic aromatic hydrocarbon; identified in air and water emitted from various combustion and pyrolysis sources (NHMRC, NRMMC 2011)
Caffeine	Acts as a stimulant in the body; a useful marker of human waste contamination in water (Sosiak and Hebben 2005)
2,4-D	2,4-Dichlorophenoxyacetic acid is a systemic herbicide used for the control of broad-leaf and aquatic weeds (NHMRC, NRMMC 2011)
Estrogens	Endogenous female hormones including estrone (E1), estradiol (E2) and estriol (E3) (Sosiak and Hebben 2005, Chen et al. 2006). Animal wastes can contribute hormones to surface runoff (Tyler et al. 2009). Both sexes of fish can be affected (El-Alfy and Schlenk 2002) as well as other aquatic organisms
Ethinylestradiol	Synthetic estrogen (ovulation inhibitor) found in birth control pills (Sosiak and Hebben 2005)
Glyphosate	A non-selective herbicide used to control weeds in agriculture industry, forestry, and the aquatic environment (NHMRC, NRMMC 2011)
Microcystin	One of the 2 main types of toxins produced by Cyanobacteria; possible carcinogen and may cause liver damage (Fischer et al. 2001, NHMRC, NRMMC 2011)
PBDE	Polybrominated diphenyl ethers are chemicals used as flame retardants in furniture, mattresses, and electronics etc.; potentially harmful to neonates (being phased out in Canada)
Sulfamethazine	A sulfonamide antibiotic ("sulfa drug"); used more frequently than all other sulfonamides in veterinary medicine; used to promote weight gain in food animals (Sosiak and Hebben 2005)
Sulfamethoxazole	A sulfonamide antibiotic ("sulfa drug"); treats bacterial and protozoan infections; often administered with trimethoprim in humans (Sosiak and Hebben 2005)
Testosterone	Endogenous male androgen (Sosiak and Hebben 2005)
Triclosan	An antimicrobial ingredient added to many consumer products (clothing, kitchenware, furniture, toys, soaps, toothpastes, cosmetics etc.; USFDA 2010)

Table 2. Locations for sample collection in the South Saskatchewan River, the Seven Persons, Bullshead, and Ross creeks, and the Medicine Hat Wastewater Treatment Plant (WWTP), with the corresponding longitude and latitude.

Sample Location	Sample Site	Longitude	Latitude
1. Seven Persons Creek upstream	Desert Blume	49°59′31.5″	110°44′0.6″
2. Seven Persons Creek downstream	Industrial Ave	50°01′44.8″	110°38′46.1″
3. Ross Creek upstream	Bridge	50°00′16.9″	110°35′6.5″
4. Ross Creek downstream	Industrial Ave	50°01′38.7″	110°38′17.8″
5. Bullshead Creek	Golf Course	49°59′22.6″	110°37′22.4″
6. South Saskatchewan River upstream – Water treatment plant	Trans-Canada Hwy	50°05′33.8″	110°39′50.9″
7. South Saskatchewan River downstream	11th Ave; CFL	50°02′28.6″	110°43′13.8″
8. Medicine Hat WWTP raw	Headwater	50°02′58.3″	110°38′19.6″
9. Medicine Hat WWTP treated	Effluent	50°03′07.4″	110°38′36.3″

the day of sampling, and all tests were completed within 96 h of sample collection. Raw wastewater samples were composites collected over a 24 h period.

Analysis

Measurements of analytes took place using ELISA procedures according to the manufacturer's instructions (Abraxis LLC, Warminster, PA). The sample volumes used for ELISA method ranged from 50 to 100 µL depending on the kit used. Absorbance was read within 15 min using an ELx808 Absorbance Microplate Reader (BioTek Instruments, Inc.) set at 405 nm. Standard curve linear regression R^2 values below 0.95 or internal control standards deviating beyond the specified kit limits resulted in data elimination. Results were considered to be below or above the detection limit when the absorbance value was less than or exceeded the lowest or highest concentration standard. If analysis of the internal standard exceeded the specified range, the data from that analytical batch were eliminated.

Validation of data

Internal standards were provided with all kits except benzo(a)pyrene, avermectins, and PBDE and were used to validate each analytical batch of samples. Replicate analyses of benzo(a)pyrene (Supelco) and avermectins (AccuStandard) were prepared using stock solutions diluted with 10 Megohm pure water (Thermo-Fisher) to concentrations that fell within the range of the kit standards. PBDE was dropped early in the study because no samples tested above the method detection limit. In addition to internal standard validation, 6 duplicate samples were submitted to ALS laboratories in Calgary for analysis of a wide range of trace organic compounds including most of the analytes used in this study. Alkylphenols, caffeine, sulfamethazine, sulfamethoxazole, testosterone, estrogens, and glyphosate were analyzed using LC/MS (USEPA Method EPA 549.2). Samples for caffeine, estrogens (EPA 549.2 MODIFIED), testosterone (EPA 549.2 MODIFIED), and glyphosate (MOE E3415 MODIFIED) were filtered and aliquoted prior to analysis. Benzo(a)pyrene and 2,4-D were analyzed via GC/MS (USEPA Method

SW846 8270). Sample extraction and concentration of benzo(a)pyrene was completed prior to analysis. The ELISA (Envirologix Quantiplate Kit Cat. EP0222) method was used for microcystin detection.

Results

Analysis

The analytical results were summarized (Table 3) by reporting the median and maximum values detected that fell within the working range of the standards. All data, including those above and below the standard range, are reported in the supplemental tables. The median values for estrogens, ethinylestradiol, 2,4-D, alkylphenol, PBDE, and sulfamethazine were always below the concentration of the lowest standard in the kits at all sites except for untreated wastewater. The same was true for sulfamethoxazole in the streams, and its concentration in the South Saskatchewan River was always close to the lower limit. Concentrations of avermectins, benzo(a)pyrene, caffeine, glyphosate, microcystins, testosterone, and triclosan at all sites were nearly always found to be within their analytical range. Analyte concentrations were similar in the tributaries and South Saskatchewan River with the exception of glyphosate, which tended to be lower at both sampling points in the river. Both treated and untreated wastewater always contained quantities of all of these analytes within or above the limits of the standards.

Validation of data

Agreement of the analytical results with the acceptable range of the internal standards (when provided) was generally good, although the results exceeded the confidence

Table 3. Summary of analytical results, concentrations are in (ng/L). The range of standards in (ng/L) is given below analyte heading. u/s = upstream; d/s = downstream.

Analyte		Seven Persons Cr. u/s	Seven Persons Cr. d/s	Ross Cr. u/s	Ross Cr. d/s	Bullshead Cr.	South Sask. River u/s	South Sask. River d/s	WWTP raw	WWTP treated
Estrogens	*n*	13	13	11	11	8	12	13	13	12
50–3000	Median	<50	<50	<50	<50	<50	<50	<50	527	<50
	Max conc	64	116	<50	<50	73	57	<50	1007	174
Ethinylestradiol	*n*	13	13	11	11	8	12	13	13	13
50–3000	Median	<50	<50	<50	<50	<50	<50	<50	<50	<50
	Max conc	<50	<50	<50	<50	<50	361	270	<50	<50
2,4 D	*n*	14	14	12	12	10	13	13	14	13
2000–8000	Median	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000
	Max conc	<2000	3010	<2000	3848	2928	5001	<2000	3749	2213
Alkylphenol	*n*	12	12	11	10	8	12	12	12	11
5000–500 000	Median	<5000	<5000	<5000	<5000	<5000	<5000	<5000	13 504	<5000
	Max conc	<5000	<5000	<5000	<5000	<5000	<5000	<5000	95 981	5145
Avermectins	*n*	14	14	12	12	9	13	14	14	13
185–15 000	Median	1978	2104	2226	2089	1624	2120	2088	2293	1495
	Max conc	5540	5909	5656	5797	3221	4205	4528	4824	5315
Benzo(a)pyrene	*n*	12	11	11	10	9	12	13	13	11
250–5000	Median	1565	1490	1466	1460	1137	1171	1479	2053	1278
	Max conc	562	644	551	562	523	568	598	747	514
Caffeine	*n*	12	12	12	10	10	12	12	12	12
175–5000	Median	<175	224	176	256	268	<175	189	15 982	962
	Max conc	649	3844	448	2550	4158	565	605	>15 000	2203
Glyphosate	*n*	13	13	12	11	10	13	14	14	12
75–4000	Median	161	209	109	305	172	<75	79	1952	433
	Max conc	304	1392	305	2578	1516	141	212	>4000	1380
Microcystins	n	14	14	12	12	10	13	14	14	13
150–5000	Median	<150	<150	<150	150	170	<150	<150	<150	<150
	Max conc	166	640	<150	1004	824	<150	275	465	<150
PBDE	*n*	6	6	6	4	2	6	6	6	6
40–4000	Median	<40	<40	<40	<40	<40	<40	<40	<40	<40
	Max conc	<40	<40	<40	<40	<40	<40	<40	41	<40
Sulfamethazine	*n*	13	13	12	11	10	13	14	14	13
50–5000	Median	<50	<50	<50	<50	<50	<50	<50	<50	<50
	Max conc	51	<50	<50	<50	<50	75	58	150	<50
Sulfamethoxazole	*n*	13	13	12	11	10	13	13	13	12
25–1000	Median	<25	<25	<25	<25	26	30	27	1112	519
	Max conc	181	53	104	48	43	82	68	>1000	>1000
Testosterone	*n*	14	14	12	12	10	13	14	14	13
8–2000	Median	9	8	12	7	8	<8	<8	1731	10
	Max conc	26	15	20	20	18	14	37	>2000	23
Triclosan	n	13	13	12	11	8	12	13	14	13
50–5000	Median	93	93	135	105	148	117	122	3955	495
	Max conc	546	352	268	378	163	226	500	>5000	2418

intervals provided with the standards by <10% on 5 of 24 occasions, and these data were included. The concentration of benzo(a)pyrene prepared in-house was 2500 ng/L, and analysis of 7 replicates resulted in a mean (mean [standard deviation]) detection of 2605 (404) ng/L. Similarly, analysis of 6 avermectins replicate standards prepared at 2000 ng/L resulted in a mean of 2009 (201) ng/L.

Validation of results by inter-lab comparison (Table 4) was only partially successful because of the frequent occurrence of analytical values outside the effective range of the methods used, usually below the detection limit. Concentrations of hormones (estrogens, ethinylestradiol, and testosterone) generally agreed in the 6 duplicate samples, although the LC/GC/MS values for raw wastewater were sometimes unexpectedly low. ELISA results for benzo(a)pyrene deviated considerably from LC/GC/MS data, possibly because of cross-reactivity of the antibodies with closely related molecules. ALS laboratories reported the concentrations for total nonylphenol ethoxylates, whereas the Abraxis method tested for nonylphenol, octylphenol, and both of their ethoxylates. There was reasonable agreement between the 2 laboratories for the antibiotics sulfamethoxazole and sulfamethazine, although the concentrations were notably low in river and creek samples as found by Shelver et al. (2008). Microcystin and caffeine concentrations were usually in accord, although the concentrations in wastewater were in excess of the maximum limit by ELISA for caffeine.

Discussion

Surface waters

The concentrations of hormones (estrogens, ethinylestradiol, and testosterone) measured in streams and the South Saskatchewan River were always below their detection limits (Table 3; supplemental figures). The same was true for alkylphenol and PBDE but not for benzo(a)pyrene, which was almost always above 1000 ng/L in the river and streams. Three of the validation samples analyzed by ALS were taken from the South Saskatchewan River at the same site and date, and no concentrations above their detection of 5 ng/L were found. The high numbers found by ELISA analysis were probably caused by cross-reactions with other polycyclic aromatic hydrocarbons of unknown origin, so our measurements are most likely overestimates. Filtering the samples might have brought our results down to the ALS range, but because we were interested in the total exposure to aquatic organisms we analyzed unfiltered samples. Low PBDE concentrations suggest low risk for aquatic mammals and top predators such as bald eagles, as found by Dornbos et al. (2015) in the

Table 4. Comparison of analytical results for selected samples between this study and ALS laboratories. ND = not determined. WWTP = wastewater treatment plant; WTP = water treatment plant.

	Detection limit		WTP treated		WTP raw		WWTP raw		WTP raw		WWTP raw		WTP raw	
	ng/L	ng/L	28 Dec 12		28 Dec 12		06 Aug 13		06 Aug 13		30 Dec 13		30 Dec 13	
Analyte	ALS	This study	ALS	This study	ALS	This study	ALS	This study	ALS	This study	ALS	This study	ALS	This study
Estrogens	10	50–3000	<10	<50	<10	<50	<10	681	<10	<50	<10	741	<10	<50
Ethinylestradiol	50	50–3000	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
2,4 D	500–5000	2000–80 000	<500	<2000	<500	2338	<5000	<2000	<500	<2000	<500	<2000	<500	<2000
Alkylphenol	2000	5000–500 000	<2000	<5000	<2000	<5000	6200	16 140	<2000	<5000	5500	95 981	<2000	<5000
Benzo(a)pyrene	5–50	250–5000	5.7	1904	<5	1160	<12	2053	<5	1583	<50	3249	<5	1671
Caffeine	5	175–5000	16.2	ND	34.3	ND	85 800	>5000	27.1	<175	145 000	>5000	75.3	308
Glyphosate	5000	75–4000	<50 000	<75	<5000	<75	9900	>4000	<5000	76	<5000	167	<5000	86
Microcystin	140–200	150–5000	<140	<150	<140	<150	<200	<150	<200	<150	<200	<150	<200	<150
Sulfamethaxazole	2	25–1000	<2	36	353	75	946	1112	10.9	33	1500	>1000	27	82
Sulfamethazine	5	50–5000	<5	<50	<5	75	<5	<50	<5	<50	<5	54	<5	<50
Testosterone	10	8–2000	<10	9	<10	8	<10	1417	<10	<8	46	>2000	<10	<8

Great Lakes ecosystem. Sulfamethazine and sulfamethoxazole were mostly below the detection limit, but sulfamethoxazole was occasionally measurable at concentrations >1000 ng/L in the summer months by both ELISA and in 3 ALS validation samples. Avermectin and triclosan concentrations were always found to be well above their detection limit, possibly from human and animal wastes, but because neither was included in the ALS validation data, this result remains unconfirmed.

The herbicides 2,4-D and glyphosates were highest in late summer, especially in Ross Creek, which drains both urban and rural land, consistent with their seasonal application. Concentrations of both were lower in the South Saskatchewan River, but only glyphosate was usually detected within the working range of the standards. Microcystins were usually below the detection limit except in late summer at all surface water sites coincident with peak algal growth. The overall trend for all of these analytes is higher concentrations in later summer as shown by caffeine, which is not a compound causing concern but is a good indicator of human activity. The tendency to increase later in the year occurs because stream and river discharge drops rapidly after the spring to early summer freshet leading to higher concentrations, even if inputs were constant. Overall, there was no obvious influence of either urban or rural inputs as measured by upstream and downstream samples in the streams and rivers, supporting the hypothesis that decreasing discharge is mostly responsible for seasonal peak concentrations.

Flood conditions did not strongly affect analyte concentrations, even though creek and especially river discharge increased by >10-fold over a short period. Fieldwork during the actual days of the flood intervals was too dangerous, but sampling was possible within a week of the river crest in both 2013 and 2014. The Ross Creek sewage lift station failed during the 2014 flood event, resulting in the discharge of raw sewage to the river for approximately 3 weeks, but the WWTP itself was unaffected. This event may have been responsible for a coincident spike in the triclosan concentration at the downstream river site. Triclosan did not increase in the downstream Ross Creek sample, but the sampling site is upstream of the lift station. No other analyte concentrations increased, including caffeine, which should also have risen if raw sewage release was responsible. The source of the floodwaters was snowmelt, exacerbated by heavy rainfall in the mountains and foothills where the South Saskatchewan River tributaries originate. Heavy flooding occurred in Calgary and some in Lethbridge, but these urban centers are 150 to 300 km upstream of the study area. If any unusual input was caused by flooding in their catchment areas, it was obscured by dilution or lost to abiotic and biotic activity in the river.

Other studies have typically reported concentrations of pharmaceutical compounds in surface waters, groundwater, and partially treated water to be <100 ng/L (median concentrations are commonly used) and <50 ng/L in treated water (WHO 2012). Although this is generally true for most prescription drugs, the range in concentrations for other trace organic compounds of concern is much larger. A literature survey revealed results often below 1 µg/L or below methodological detection limits, but others were high enough to be reported in milligrams per liter, especially microcystins and caffeine (Table 4). Comparison is difficult because of differing analytical methodology, statistical analyses, and means of reporting data, but the data presented here are broadly consistent with other studies and tend to be at the low end of the ranges reported in the literature.

Drinking water is only one potential route of exposure according to Stanford et al. (2010) in their investigation of the relative exposure of estrogenic compounds from different sources. Animal wastes can contain trace organic compounds, particularly antibiotics and herbicides. Kruger et al. (2013) reported that glyphosate concentrations in the urine of Danish cows ranged from 10 to 100 µg/L and noted that genetically modified food is probably exposed to glyphosate. Mortl et al. (2013) reported that agricultural use influences glyphosate occurrence in Hungarian waters. This problem may be reduced with pharmaceutical and personal care products in wastewater used to irrigate vegetables; Wu et al. (2014) found that the annual exposure of humans consuming salad, root vegetables, and cabbage was only 3.7 µg per capita in California. Trost et al. (2013) obtained similar results using the same methodology as our current study for sulfamethazine, sulfamethoxazole, and 17β-estradiol applied to bare soil, corn, hay, and prairie plots in Minnesota. Kromrey (2009) concluded that the treated effluents from both the Lethbridge and Medicine Hat wastewater treatment plants have the potential to alter the reproductive success of fathead minnows (*Pimephales promelas*) in the South Saskatchewan River based on laboratory studies and the data of Sosiak and Hebben (2005), but effluent concentrations of nonylphenol ethoxylates (measured as alkylphenols in the current study) seem to have been much higher in 2005.

Influence of wastewater

Data from Environment Canada (2015) and the City of Medicine Hat from June 2012 to December 2013 show that <2% of the discharge in the South Saskatchewan River below Medicine Hat was treated effluent (0.02–0.34%) or tributary water (0.1–1.3%) during this period (Fig. 2). The discharge of treated effluent is fairly constant, but the flow in the river and tributaries both vary by about an order

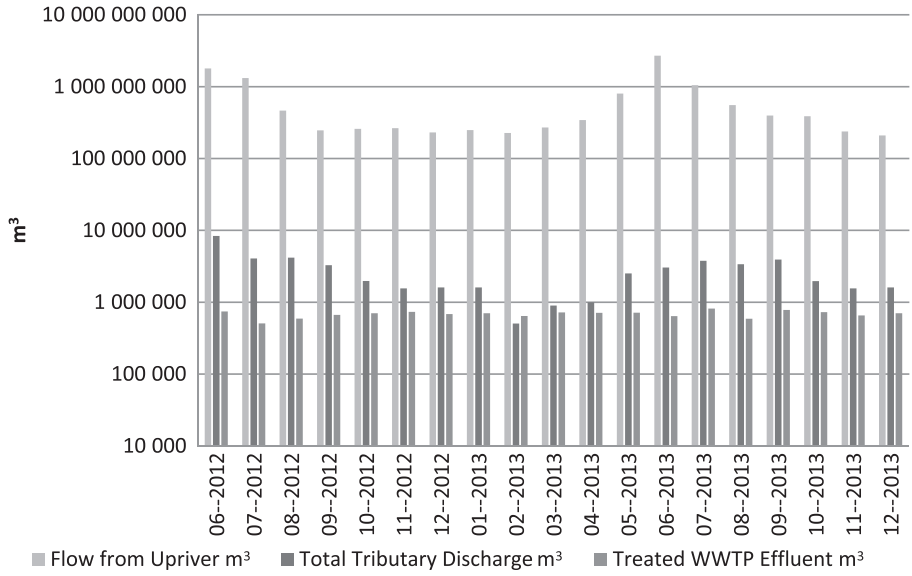

Figure 2. Composition of river water based on monthly discharge downstream of Medicine Hat, Alberta, from June 2012 to December 2013.

of magnitude from winter low flow to spring runoff. On a volume basis, the influence of Medicine Hat's treated effluent and the tributaries is therefore notably small, even when river flow is low. Seasonal rainfall events could alter these proportions, but no large rainstorms coincided with sampling dates.

The highest concentrations of all analytes were found in raw sewage, but the median levels of ethinylestradiol, 2,4-D, microcystins, PBDE, and sulfamethazine were below the lower detection limit of the ELISA analysis (i.e., below the concentration of the lowest standard). Treated wastewater contained lower concentrations of analytes than raw sewage, and the amount of reduction varied from 22% to 99% (Table 5) based on the mean values from 11 to 14 samples taken over a 3-year period. The removal rates for ethinylestradiol, PBDE, and sulfamethazine are not meaningful because their concentration in the raw wastewater was so low. Generally, the rate of removal was highest for hormones, caffeine, alkylphenol, triclosan, and glyphosate and lowest for 2,4-D, benzo(a)pyrene, and antibiotics. These findings are consistent with those reported by Williams et al. (2014) who summarized the effectiveness of various methods of wastewater treatment for a variety of trace organic compounds.

Analysis of the 6 duplicate samples by GC/MS revealed a wide variety of compounds in the following categories; polycyclic aromatic hydrocarbons, herbicides, pesticides, pharmaceuticals and personal care products, organic parameters, and miscellaneous substances including hormones, but the great majority of analytes were present below their detection limits. A number of drugs occurred in raw wastewater at concentrations <1 µg/L, but others were present in higher concentrations (Table 6).

Alkylphenols, testosterone, and estrogens were removed at high rates (estimated 91–97%) by the Medicine Hat WWTP. The reduction in steroid hormones and endocrine disrupting compounds possibly resulted from UV treatment, but the data are insufficient to reach a firm conclusion. The effect of pesticides in irrigation canals may also be significant but would occur upstream of Medicine Hat. A chronic toxicity study with *Daphnia magna*, an important zooplankton in aquatic environments, showed that the concentrations of testosterone in Medicine Hat's treated wastewater are far below threshold levels that reduce fecundity and fertility in these crustaceans (Barbosa et al. 2008).

A potential issue arises with exposure of soil and aquatic microorganisms to antibiotics in treated effluent. The World Health Organization prepared a report summarizing the issue and gaps in knowledge (WHO 2014) for all aspects of antimicrobial resistance, of which water is only a small part. Treating the final effluent by UV irradiation to reduce the microbial population in wastewater before discharging to the lagoons is beneficial (Williams et al. 2014). The results of our current study suggest that the contribution of the WWTP in Medicine Hat to the South Saskatchewan River is small, but few biotic data are available to assess the potential impact.

Guidelines

Guidelines for safe water quality concentrations of most trace organic compounds of interest are generally lacking. Separate guidelines for drinking water, wastewater effluent, agricultural use (irrigation and livestock), recreational use, and aquatic life (both freshwater and marine) would

Table 5. Comparison of data found in this study to literature values. All results are median values in (ng/L) unless otherwise indicated. BDL – below detection limit. ML – multiple locations. Rivers in Alberta unless stated otherwise. u/s – upstream. d/s – downstream.

Water Source	17α Estrogens	17αEthinyl estradiol	2,4-D	Alkylphenol	Avermectins	Benzo(a)pyrene	Caffeine	Reference
Medicine Hat WWTP treated	26	5	1022	255	1655	1278	962	This study
Medicine Hat WWTP treated				2800			872	Sosiak and Hebben (2005)
Calgary Fish Cr. WWTP treated	BDL	8.5		2820–7680			670	Sosiak and Hebben (2005), Chen et al. (2006)
Calgary Bonnybrook WWTP treated	BDL	2.6		1650, 98–3440			405	ibid
Lethbridge WWTP treated	BDL	BDL		200			74	Sosiak and Hebben (2005)
Milwaukee WWTP treated	BDL						67	Blair et al. (2013)
UK WWTP treated	1.4–1.7	0.4–3.4						Williams et al. (2003)
ML - WWTP raw							5–200 000	Sodre et al. (2010)
ML - WWTP treated							8–20 000	Sodre et al. (2010)
ML - WWTP treated	6.4–12.6	0.6–5.6						Pal et al. (2010);
ML - WWTP treated	3							Vidal-Dorsch et al. (2012)
S. Saskatchewan R. d/s Medicine Hat	11	4	631	157	2263	1479	189	This study
S. Saskatchewan R. u/s Medicine Hat	BDL	BDL		110			466	Sosiak and Hebben (2005)
Bow R. u/s Calgary				37			160	Chen et al. (2006)
Bow R. d/s Calgary				313			64	Chen et al. (2006)
Elbow R. u/s Calgary				66			120	Chen et al. (2006)
US streams	30	7.3		80		40	100	Kolpin et al. (2002)
Lake Michigan							71	Blair et al. (2013)
Rivers Nene and Lea, UK, d/s WWTP	1.2							Williams et al. (2003)
Carrot R., Saskatchewan			8.5					Environment Canada (2013)
Assiniboine R., Saskatchewan			21.5					Environment Canada (2013)
Red R., Manitoba			43.5					Environment Canada (2013)
ML - raw surface water							5–1000	Sodre et al. (2010)
ML - drinking water							5–100	Sodre et al. (2010)
ML - surface water	25	1.5–4.7						Pal et al. (2010)
UK groundwaters (max conc)							4500	Stuart et al. (2010)
Pennsylvania streams	0.43						6–517	Reif et al. (2012)
Surface waters in France						270		Gasperi et al. (2009)
Pearl R. estuary, China								Guan et al. (2009)
Liao R., China	7.4			52.1				Wang et al. (2011)
Alberta streams			31					Phelan (2012)
Alberta streams					2–210			Den Heever (2006)
Ontario streams					6.2–1172			Den Heever (2006)
Water Source	Glyphosate	Microcystins	PBDE	Sulfamethoxazole	Sulfamethazine	Testosterone	Triclosan	Source
Medicine Hat WWTP treated	433	62	BDL	21	519	10	495	This study
Medicine Hat WWTP treated				BDL	363	BDL		Sosiak and Hebben (2005)
Calgary Fish Cr. WWTP treated				BDL, 377	415	BDL		Sosiak and Hebben (2005), Chen et al. (2006)
Calgary Bonnybrook WWTP treated				427, 72	931	BDL		ibid
Lethbridge WWTP treated				BDL	886	BDL		Sosiak and Hebben (2005)
Milwaukee WWTP treated				BDL	29	6.4	5	Blair et al. (2013)
North Dakota WWTP treated					1200			Shelver et al. (2008)
ML - WWTP treated					2–2800	1.3–30		Pal et al. (2010)
ML - WWTP treated					20–2000	10	790	Vidal-Dorsch et al. (2012)
S. Saskatewan R. d/s Medicine Hat	79	69	BDL	15	27	7	122	This study
S. Sasktchewan R. u/s Medicine Hat					101	BDL		Sosiak and Hebben (2005)
US streams				220	66	116	140	Kolpin et al. (2002)
Lake Michigan				BDL	16	6.4	5	Blair et al. (2013)
Hungarian agricultural streams	120–1000							Mortl et al. (2013)

(*Continued*)

Table 5. (*Continued*).

Water Source	17α Estrogens	17αEthinyl estradiol	2,4-D	Alkylphenol	Avermectins	Benzo(a)pyrene	Caffeine	Reference
Hungarian non-agricultural streams	35–64							Mortl et al. (2013)
Red R., North Dakota					60			Shelver et al. (2008)
Llobregat River, Spain					1100			Ginebreda et al. (2009)
Bow R. u/s of Calgary				2–21	BDL			Chen et al. (2006)
Bow R. d/s of Calgary				48	BDL			Chen et al. (2006)
Elbow R. u/s of Calgary				4.4	BDL			Chen et al. (2006)
ML - surface water					7–2000	4.3–16		Pal et al. (2010)
UK groundwaters (max conc)							2110	Stuart et al. (2010)
Arkansas streams					361			Haggard et al. (2006)
ML - surface water					0.5–7.3			Vidal-Dorsch et al. (2012)
Pennsylvania streams					5–146			Reif et al. (2012)
US lakes with algal blooms		1000						Davis et al. (2009)
Lake Erie, Ontario		0.4–21 000						Rinto-Kanto et al. (2009)
California lakes		100–500 000						Backer et al. (2009)
Multiple Canadian lakes		150–2 153 000						Orihel et al. (2012)
Pearl R. estuary, China			0.1–65					Guan et al. (2009)
Liao R., China							81.3	Wang et al. (2011)
Alberta streams				2–11				Den Heever (2006)
Ontario streams				0.3–408				Den Heever (2006)

Table 6. Mean removal efficiency of Medicine Hat's wastewater treatment plant. Concentrations of analytes are in (ng/L).

Analyte	Raw sewage	Treated sewage	% Reduction
Testosterone	1788	11	99
Alkylphenol	27 817	779	97
Caffeine	16 799	1108	93
PBDE	14	1	93
Estrogens	545	48	91
Triclosan	6139	677	89
Glyphosate	2464	554	78
Microcystins	143	65	55
Sulfamethazine	32	21	34
2,4-D	1629	1129	31
Benzo(a)pyrene	1890	1354	28
Ethinylestradiol	8	6	25
Avermectins	3006	2337	22
Sulfamethoxazole	1175	914	22

Table 7. Drugs found in raw wastewater samples analyzed by ALS Laboratories. Concentrations in µg/L.

Drug	6 Aug 13	30 Dec 13	Use
Acetaminophen	71.8	73.7	Analgesic
Atenolol	2.02	0.345	Angina, hypertension
Benzoylecgonine		1.13	Main metabolite of cocaine
Ciprofloxacin	6.96	7.51	Antibiotic
Codeine	3.54	2.76	Analgesic
Cotinine	2.36	0.745	Nicotine metabolite, tobacco
Dehydronifedipine	2.36	0.021	Metabolite of nifedipine, Angina, hypertension
Diclofenac	3.47	4.26	Anti-inflammatory, arthritis
1,7 dimethylxanthine		21.2	Metabolite of caffeine
Diphenhydramine	0.48	1.33	Antihistamine
Furosemide	0.492	1.15	Diuretic, cardiac failure, edema
Hydrochlorothiazide	3.03	6.03	Diuretic, hypertension
Ibuprofen	14.1	18.5	Analgesic, anti-inflammatory
Metformin	85.5	91.8	Type 2 diabetes
Naproxen	10.7	13.0	Anti-inflammatory, arthritis
Norfloxacin		1.96	Antibiotic
Ofloxacin		1.42	Antibiotic
Ranitidine	1.22	2.02	Inhibits stomach acid, ulcers

all be useful. Issues surrounding guidelines include toxicity, antimicrobial resistance, and reproductive effects in aquatic organisms, humans, and animals. Anderson et al. (2012) provide an excellent review used to develop a monitoring strategy for the State of California. Other useful government sources of information are the Guidelines for Canadian Drinking Water Quality (Health Canada 2012), the World Health Organization (2012), and the Canadian Chemicals Management Plan (www.chemicalsubstances.gc.ca). A detailed analysis of the development of guidelines for chemicals of emerging concern is beyond the scope of this study, but some guidelines exist for the analytes measured (Tables 7 and 8). More data are available for other compounds, and provisional guidelines for a wide variety of trace organic compounds of concern

Table 8. All currently available international water guidelines (µg/L) for the compounds analyzed in this study. Includes guidelines from Australia, Canada, United States, Europe, and the World Health Organization.

	Australia							
Chemical	Recycled water[a]	Health[b]	Drinking water[c]	Canada[d]	WHO[e]	US[f]	US[g]	Europe[h]
2,4-D	30	30	0.1	100/4	30	100	70	0.1
Glyphosate	–	1000	10	280	–	–	700	0.1
Benzo(a)pyrene	0.01	0.01	–	0.01	0.7	0.0038	0.2	0.01
Microcystins	–	1.3	–	1.5	1	–	–	–
Sulfamethoxazole	35	–	35	–	–	–	–	–
Ethinylestradiol	0.0015	–	0.0015	–	–	–	–	–
Estriol	0.05	–	0.05	–	–	–	–	–
Estrone	0.03	–	0.03	–	–	–	–	–
Testosterone	7	–	7	–	–	–	–	–
Sulfamethazine	35	–	35	–	–	–	–	–
Estradiol	0.175	–	0.175	–	–	–	–	–
4-Nonylphenol	500	–	500	–	–	–	–	–
Triclosan	0.35	–	0.35	–	–	–	–	–
Caffeine	0.35	–	0.35	–	–	–	–	–

[a]guidelines for water recycling (EPHC, NHMRC, NRMMC 2008).
[b]based on human health concerns; levels in drinking water should not exceed this (NHMRC and NRMMC 2011).
[c]based on the analytical limit of determination; if pesticide is detected at or above this value the source should be identified and action should be taken to prevent further contamination (NHMRC and NRMMC 2004).
[d]guidelines for drinking water quality based on health; listed as a maximum acceptable concentration (MAC; Health Canada 2012).
[e]guidelines for chemicals that are of health significance in drinking water (WHO 2012).
[f]recommended surface water quality criteria for the protection of human health in regards to the consumption of water and organism (USEPA 2013a).
[g]the highest level of a contaminant allowed in drinking water; listed as a maximum contaminant level (MCL; USEPA 2013b).
[h]guidelines for water quality intended for human consumption (EU 1998).

in drinking water have been published by Schriks et al. (2010) or may be found in the publications of the World Health Organization (WHO 2011, 2012; WHO/UNEP 2013). Improvements in analytical methodology will make guideline development more feasible but cost will continue to be an issue. The methodology employed by our current project combined with the assumption that representative compounds make useful monitoring tools can aid this process.

The top 3 research priorities identified by a survey of 535 environmental scientists from 57 countries were to (1) determine the effects of long-term exposure to low concentrations of pharmaceuticals and personal care product mixtures on non-target organisms, (2) develop effluent treatment methods to reduce the effects of pharmaceutical and personal care products in the environment while not increasing the toxicity of whole effluents, and (3) assess the environmental risks of metabolites and environmental transformation products of these compounds (Rudd et al. 2014). The safe disposal of pharmaceutical and personal care products and other organic chemicals is an issue at all levels of government that affects the transport of chemicals into the environment. Currently, consistent programs are lacking for pick-up and disposal of medications. Public awareness and education can discourage disposal of drugs in the garbage or down the toilet (NAPRA 2009). Further environmental contamination would benefit from the implementation of a widespread, uniform program for the return and disposal of expired, discontinued, and unused drugs.

Methods for analysis

Although GC/MS has high separation efficiency, high speed, and lower matrix effect, it often requires derivatization and is applicable only to volatile agents (Fang et al. 2016). LC/MS does not require derivatization and has good sensitivity, specificity, and versatility but is complex, requires high sample and solvent volumes, is time-consuming, and is subject to matrix effects (Fang et al. 2016, Guo et al. 2017). In contrast to LC/GC/MS methods, the ELISA is rapid, simple, and cost effective (Gan and Patel 2013, Fang et al. 2016). In addition, ELISA tends to have a higher sensitivity and can analyze large sets of samples (Fang et al. 2016). A limitation of this method is the potential overestimation of the result (Gan and Patel 2013). One way this can occur is through cross-reactivity with closely related molecules (Gan and Patel 2013, Fang et al. 2016). Another issue is that in a competitive ELISA the absorbance–concentration calibration curve is only linear within a range limited by the competition of the analyte and the enzyme-conjugate for binding sites on the monoclonal antibody attached to the well. When little or no analyte is present, the color development is intense because a large amount of enzyme-conjugate remains bound to the wells to react with the chromogenic substrate. The opposite is true when the concentration is high; high concentrations may be underestimated because little or no enzyme-conjugate remains in the wells after washing. The enzymatic color reaction is also time-dependent, and prolonged incubation may overemphasize results (Gan and Patel

2013). Ideally, no single analytical method should be relied on, and the best use for ELISA may be as a screening tool to indicate problems requiring further investigation using more costly methods.

Conclusions

- The ELISA-based kits were an economical and accurate alternative to classical analytical methods with the following limitations:
  - not all kits include internal standards,
  - cross-reactions with related compounds may occur leading to overestimation of results, and
  - it is assumed that a select group of representative chemicals will be an effective monitoring tool for trace organic compounds.
- Wastewater treatment at Medicine Hat removes indicator analytes with efficiencies ranging from 22% to 99%.
- Less than 2% of the discharge in the South Saskatchewan River below Medicine Hat was treated effluent (0.02–0.34%) or tributary water (0.1–1.3%) in the study period.
- Polybrominated diphenyl ethers and ethinylestradiol concentrations were usually at or below the limit of detection.
- All other analytes were found at concentrations consistent with those reported in other studies for surface water and wastewater.
- The herbicides 2,4-D and glyphosate generally increased in concentration over the summer in the wastewater and tributary samples, and on one occasion in the river, consistent with the seasonal pattern of their use.
- Microcystin concentrations were highest in the summer.
- Avermectins, benzo(a)pyrene, alkylphenol, and caffeine concentrations tended to increase under low flow conditions.
- Analyte concentrations did not increase or decrease consistently in either the tributaries or the South Saskatchewan River after passing through Medicine Hat.
- Flood conditions in the South Saskatchewan River did not cause any major changes in the concentration of the indicator analytes.

Disclosure statement

No potential conflict of interest was reported by the authors.

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