

**A Preliminary Survey of Pharmaceuticals
and Endocrine Disrupting Compounds in
Treated Municipal Wastewaters and
Receiving Rivers of Alberta**

A Preliminary Survey of Pharmaceuticals and Endocrine Disrupting Compounds in Treated Municipal Wastewaters and Receiving Rivers of Alberta

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EXECUTIVE SUMMARY

Pharmaceuticals, hormones, and other known or suspected endocrine disrupting compounds (EDCs) have been widely detected in various waters throughout the world. Prior to this study, however, sampling for these substances was rather limited within Alberta. In 2002 and 2003, due to concerns about potential impacts on humans, livestock, aquatic organisms, and wildlife, Alberta Environment collected wastewater treatment plant (WWTP) effluents and receiving river water from numerous locations throughout the Province and analysed them for a broad range of organic wastewater contaminants (OWCs). This initial survey, encompassing an assortment of pharmaceuticals, antibiotics, steroids, surfactants, and plasticizers, was designed to determine which compounds are released by WWTPs in Alberta and to assess their presence in receiving river waters.

Results of this study indicate that many of the 105 compounds and isomer mixtures that were tested for occur with some regularity in Alberta WWTP effluents and can be detected in the associated receiving rivers. In the majority of cases, concentrations of target analytes in receiving waters at well-mixed downstream sites were either below detection or several orders of magnitude lower than the same compounds in corresponding WWTP effluents. Certain groups of pharmaceuticals, namely the quinolone and tetracycline antibiotics, were virtually absent in surface waters, while others, including acidic pharmaceuticals, neutral pharmaceuticals, and sulfonamide antibiotics, were markedly lower in rivers than they were in effluents. Similarly, those EDCs that occurred at measurable concentrations in effluents were typically much reduced or below detection in downstream river water. All of the phthalate esters, one of nine mono-phthalate esters, and all nonylphenol ethoxylates analysed were found in effluents and, albeit at greatly reduced levels, in receiving waters.

At present, surface water guidelines have not yet been established for the vast majority of compounds examined during this study. Nonetheless, the Canadian Council of Ministers of the Environment nonylphenol guideline for the protection of aquatic life (1.0 µg/L) was exceeded by 0.4 µg/L in the Oldman River. However, since toxic equivalents for each river were calculated based on data from a single sample collected at a single point in time, they should be viewed with caution. A need for additional monitoring of OWCs in Alberta's surface waters is indicated.

TABLE OF CONTENTS

EXECUTIVE SUMMARY.....	i
LIST OF TABLES	iii
LIST OF FIGURES.....	v
LIST OF APPENDICES	vi
ACKNOWLEDGEMENTS.....	vii
1.0 INTRODUCTION	1
2.0 METHODS.....	2
2.1 Analyte Selection.....	2
2.2 Site Selection and Sample Collection	2
2.3 Sample Extraction.....	3
2.4 Sample Analyses	3
2.4.1 Pharmaceuticals	3
2.4.2 EDCs.....	3
2.5 Quality Assurance.....	4
3.0 RESULTS AND DISCUSSION.....	5
3.1 Quality Assurance	5
3.1.1 Spiked Samples.....	5
3.1.2 Laboratory Blanks	5
3.2 Pharmaceuticals.....	5
3.2.1 Acidic Pharmaceuticals	6
3.2.2 Neutral Pharmaceuticals	6
3.2.3 Quinolone Antibiotics	6
3.2.4 Sulfonamide Antibiotics	7
3.2.5 Tetracycline Antibiotics.....	7
3.3 Endocrine Disrupting Compounds.....	7
3.4 Phthalate Esters	8
3.5 Nonylphenol ethoxylates.....	8
4.0 CONCLUSION	10
5.0 RECOMMENDATIONS	11
6.0 LITERATURE CITED	12
7.0 TABLES	15
8.0 FIGURES	37
9.0 APPENDICES	47

LIST OF TABLES

Table 1	Summary of acidic pharmaceuticals analysed in WWTP effluents and receiving rivers of Alberta. Details based on Karch (2003).	16
Table 2	Summary of neutral pharmaceuticals analysed in WWTP effluents and receiving rivers of Alberta. Details based on Karch (2003).	17
Table 3	Summary of antibiotics analysed in WWTP effluents and receiving rivers of Alberta. Details based on Karch (2003).	18
Table 4	Summary of endocrine disrupting compounds analysed in WWTP effluents and receiving rivers of Alberta.	19
Table 5	Summary of phthalate esters, mono-phthalate, and nonylphenol ethoxylates analysed in WWTP effluents and receiving rivers of Alberta.	20
Table 6	Summary of wastewater treatment plants (WWTPs) and river stations sampled.	21
Table 7	Acidic pharmaceutical concentrations in WWTP effluents and receiving rivers of Alberta ($\mu\text{g/L}$). Bracketed values indicate standard deviation of triplicate measurements. ND = Not Detected.	22
Table 8	Neutral pharmaceutical concentrations in WWTP effluents and receiving rivers of Alberta ($\mu\text{g/L}$). Bracketed values indicate standard deviation of triplicate measurements. ND = Not Detected.	23
Table 9	Quinolone antibiotic concentrations in WWTP effluents and receiving rivers of Alberta ($\mu\text{g/L}$). Bracketed values indicate standard deviation of triplicate measurements. ND = Not Detected.	24
Table 10	Sulfonamide antibiotic concentrations in WWTP effluents and receiving rivers of Alberta ($\mu\text{g/L}$). Bracketed values indicate standard deviation of triplicate measurements. ND = Not Detected.	25
Table 11	Tetracycline antibiotic concentrations in WWTP effluents and receiving rivers of Alberta ($\mu\text{g/L}$). Bracketed values indicate standard deviation of triplicate measurements. ND = Not Detected.	26
Table 12	EDC concentrations in WWTP effluents of Alberta (ng/L). Steroid estrogens are indicated in italics. ND = Not Detected.	28
Table 13	EDC concentrations in receiving rivers of Alberta (ng/L). Steroid estrogens are indicated in italics. ND = Not Detected.	29
Table 14	Phthalate ester concentrations in WWTP effluents of Alberta (ng/L). ND = Not Detected.	30
Table 15	Phthalate ester concentrations in receiving rivers of Alberta (ng/L). ND = Not Detected.	31
Table 16	Mono-phthalate ester concentrations in WWTP effluents and receiving rivers of Alberta (ng/L). ND = Not Detected; NA = Not Analysed.	32

Table 17	Nonylphenol ethoxylate concentrations in WWTP effluents of Alberta (ng/L).	
	ND = Not Detected.	34
Table 18	Nonylphenol ethoxylate concentrations in receiving rivers of Alberta (ng/L).	
	ND = Not Detected.	35

LIST OF FIGURES

Figure 1	Pharmaceutical concentrations in WWTP effluents of Alberta.	38
Figure 2	Pharmaceutical concentrations in receiving rivers of Alberta.	39
Figure 3	EDC concentrations in WWTP effluents of Alberta (recovery corrected data).	40
Figure 4	EDC concentrations in receiving rivers of Alberta (recovery corrected data).	41
Figure 5	Phthalate ester concentrations in WWTP effluents of Alberta (recovery corrected data). Note scale differences on y-axes.	42
Figure 6	Phthalate ester concentrations in receiving rivers of Alberta (recovery corrected data).	43
Figure 7	Nonylphenol ethoxylate concentrations in WWTP effluents of Alberta (recovery corrected data). Note scale differences on y-axes.	44
Figure 8	Nonylphenol ethoxylate concentrations in receiving rivers of Alberta (recovery corrected data). Note scale difference on y-axes.	45

LIST OF APPENDICES

Appendix I	Median recoveries of spiked surrogates from samples of WWTP effluent and receiving river water collected in Alberta.....	48
Appendix II	EDC concentrations in blank (type 1, laboratory grade) water samples.....	49
Appendix III	Phthalate ester concentrations in blank (type 1, laboratory grade) water samples.....	50
Appendix IV	Phthalate monoester concentrations in blank (type 1, laboratory grade) water samples.....	51
Appendix V	Nonylphenol ethoxylate concentrations in blank (type 1, laboratory grade) water samples.....	52

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1.0 INTRODUCTION

During the past ten to fifteen years, the presence of pharmaceuticals, hormones, and other endocrine disrupting compounds (EDCs) in wastewater treatment plant (WWTP) effluents, receiving waters, drinking water, and groundwater has become an issue of increasing international attention and concern (e.g. Sacher *et al.* 1998, McDowell and Metcalfe 2001, Kolpin *et al.* 2002, Metcalfe *et al.* 2002, Boyd *et al.* 2003, Drewes *et al.* 2003, Metcalfe *et al.* 2003a, 2004, Tauxe-Wuersch *et al.* 2005). Collectively referred to as organic wastewater contaminants (OWCs), it is probable that these compounds have been entering surface- and groundwater systems for as long as people have been using them. Since the detection of clofibric acid, a synthetic blood lipid regulating drug, in river and tap water of Berlin, Germany (Stan *et al.* 1994), work on the topic has rapidly expanded to include a variety of waters throughout the world. Subsequent research, including a monumental inventory of organic wastewater contaminants (OWCs) in United States rivers (Kolpin *et al.* 2002), has revealed a broad range of compounds that can be detected regularly in surface waters of industrialized nations, including Canada (Metcalfe *et al.* 2002). These detections, albeit largely at trace levels, are of concern due to potential impacts on humans, aquatic organisms, livestock, and wildlife.

Although OWCs in the aquatic environment may have numerous origins, it has been shown that municipal WWTPs are a major point source (Drewes *et al.* 2003). Despite removing a large proportion of pharmaceuticals and EDCs through various treatment processes (Boyd *et al.* 2003), WWTPs do not eliminate all compounds completely. Consequently, these contaminants tend to be discharged into receiving waters (Heberer 2002). Studies have shown that photodegradation (light-mediated breakdown) and biodegradation (microorganism-mediated breakdown) in the environment contribute to the reduction of OWC concentrations in surface waters (Andreozzi *et al.* 2003). However, the potential impacts of compounds that resist degradation, as well as breakdown products (metabolites) of more labile (degradable) contaminants, must be considered. Furthermore, even relatively labile substances are given persistent qualities simply through their constant reintroduction into surface waters (Daughton and Ternes 1999).

It is widely recognized that a general lack of monitoring data for many OWCs in surface waters makes accurate risk assessment extremely challenging (Jones 2001). Prior to 2002, however, work on the topic of pharmaceuticals and EDCs in the environment was rather limited within the Province of Alberta. Aside from two studies on WWTP effluents from Calgary (Metcalfe *et al.* 2003a, Simieritsch *et al.* 2004), there were no assessments of these contaminants in either effluents or surface waters of the Province. Hence, it was deemed necessary to conduct a preliminary survey of pharmaceuticals, hormones, endocrine disruptors, and other OWCs in WWTP effluents and receiving waters throughout Alberta. As a result, during 2002 and 2003, Alberta Environment (AENV) sampled treated WWTP effluent from the cities of Calgary, Edmonton, Red Deer, Lethbridge, and Medicine Hat for a broad range of OWCs. Receiving waters from the Bow, North Saskatchewan, Red Deer, Oldman, and South Saskatchewan Rivers were analysed for these same compounds. The primary intent of this initial investigation was to determine which substances are released by WWTPs in the Province and to identify the range of compounds that can be detected in receiving waters at fully mixed downstream sites.

2.0 METHODS

2.1 Analyte Selection

Pharmaceutical compounds chosen for analysis (Tables 1-3) were largely selected from a list of OWCs detected with the highest frequency and at the greatest concentrations in a fairly recent and comprehensive survey of 139 receiving streams throughout the United States (Kolpin *et al.* 2002). Additional selection criteria for pharmaceuticals were developed by the analytical laboratory (Water Quality Centre, Trent University, Peterborough, Ontario) and included: (1) a review of the drugs most commonly found in WWTP effluents and surface waters in Europe; (2) a review of the prescription patterns for drugs used in clinical applications in Canada; (3) the availability of analytical methods; and (4) the instrumentation and capability of the analytical laboratory itself. Although numerous pharmaceuticals associated exclusively with the livestock industry are also of potential concern, it was assumed that these are less likely to enter surface waters during winter, when most sampling occurred. Hence, they were not incorporated into our study.

The list of target EDCs (Table 4) and other OWCs (Table 5) was originally developed by the analytical laboratory (Institute of Ocean Sciences, Federal Department of Fisheries and Oceans, Sidney, British Columbia) based primarily on an examination of all the compounds that can potentially occur in sewage and pulp mill effluents. Selection criteria for these substances included: (1) the importance of a compound, in terms of potential aquatic and human impacts; (2) the likelihood of a compound passing through a conventional WWTP; and (3) the availability of data from comparable studies.

2.2 Site Selection and Sample Collection

Sampling sites (Table 6) were chosen to incorporate WWTPs and associated receiving rivers near areas of greatest human population in Alberta. In all but one instance, a sample of WWTP effluent and one of well-mixed downstream river water were collected. In the case of the South Saskatchewan River, river water was collected upstream of the WWTP at the request and expense of the City of Medicine Hat. Due to prohibitive costs, it was not feasible to sample upstream of the other WWTPs, nor was it possible to analyse WWTP influent. Although replication of individual samples would have resulted in statistically defensible data, it was decided that, in the interests of providing a more comprehensive geospatial picture, limited funds would be best spent on single samples from numerous sites, rather than multiple samples from only a few sites.

During the winter of 2002/2003, Alberta Environment collected grab samples of final treated effluent and river water in pre-cleaned four-litre glass bottles. Each of these bottles was subjected to a single rinse with sample water before being filled. Upon expert consultation (Dr. C. Metcalfe, Trent University), it was agreed that this pre-rinse would saturate any available binding sites on the glass, thereby preventing possible adsorption of some of the target analytes to the sampling bottles. Within 24 hours of collection, samples were sent to Envirotest Laboratories Ltd. (ETL) in Edmonton, Alberta for extraction and subsequent distribution to the appropriate analytical laboratories. All samples were stored in the dark at 4°C prior to

extraction. Since some extracts (Fish Creek WWTP effluent, Bow River water, and Red Deer River water) were lost in transit, it was necessary to resample these sites during low flows in the summer of 2003.

2.3 Sample Extraction

Due to the large volumes of water required to achieve low detection limits during analyses, it was considered impractical to ship raw water samples to the analytical laboratories. Therefore, samples were first submitted to ETL (Edmonton, Alberta) for solid phase extraction of pharmaceutical compounds, as well as dichloromethane extraction and stir bar sorptive extraction of EDCs and other OWCs. These procedures were performed in accordance with protocols provided by the analytical laboratories.

2.4 Sample Analyses

2.4.1 Pharmaceuticals

The Water Quality Centre at Trent University (Peterborough, Ontario) concentrated samples and performed triplicate analyses for pharmaceutical compounds using liquid chromatography/electrospray-tandem mass spectrometry. Method detection limits (MDL; the minimum concentration of a given compound that a particular analytical method can reliably detect in a sample) varied from 1-15 ng/L for neutral pharmaceuticals and antibiotics and from 1-25 ng/L for acidic pharmaceuticals.

2.4.2 EDCs

The Institute of Ocean Sciences (Department of Fisheries and Oceans, Sidney, British Columbia) tested samples for a broad range of OWCs, including hormones, contraceptives, plasticizers, surfactants, and other proven or suspected EDCs. Individual di-phthalate esters were analysed using a low-resolution gas chromatography mass spectrometer system (Trace GC/Voyager MS from Thermo Finnigan). Both mono-phthalate esters and isomer mixtures of di-phthalate esters were examined using a liquid chromatograph mass spectrometer system (HPLC system Beckman Model 126/ESI VG Quattro MS, Micromass), while nonylphenol, nonylphenol ethoxylates, and their associated surrogates were analysed via liquid chromatography/electrospray ionization mass spectrometry. Sterols and other EDCs were measured with a high-resolution mass spectrometer.

Method detection limits for variables analysed by the Department of Fisheries and Oceans (DFO) differed markedly among compounds and among samples, depending on the sample matrix (river water vs. effluent). EDCs and steroid estrogens in river water had MDLs from 0.018-371 ng/L, while the same analytes had MDLs from 0.019-689 ng/L in WWTP effluent. Similarly, MDLs for phthalate esters (0.01-5.7 ng/L in river water, 0.03-22.2 ng/L in effluent), mono-phthalate esters (0.6-4.9 ng/L in river water, 1.6-11.9 ng/L in effluent), and nonylphenol ethoxylates (1.78-202 ng/L in river water, 4.98-642 ng/L in effluent) varied considerably, both among analytes and among individual samples.

2.5 Quality Assurance

In keeping with the methods of Metcalfe *et al.* (2003b) and Miao *et al.* (2004), ETL extracted samples and fortified (“spiked”) the extracts with internal drug standards provided by Trent University. By including a known concentration of a particular compound, the Trent laboratory was able to construct a calibration curve, which permits the analyst to compensate for so-called “matrix effects”. Compounds that co-occur with target analytes in complex matrices (in this case, WWTP effluent and river water) have a tendency to suppress or, on occasion, enhance signals reported via liquid chromatography/ electrospray-tandem mass spectrometry. By spiking known concentrations of between three and five target pharmaceuticals, a calibration curve can be derived and used to quantify the actual target analytes (Dr. C. Metcalfe, pers. comm.).

Several laboratory blanks (used to identify potential sources of error in laboratory techniques or analytical procedures) were prepared to evaluate results obtained from the DFO laboratory. Since laboratory blanks are typically based on type 1 laboratory grade de-ionized water, analysis thereof should theoretically not result in any detections. A solvent/glassware blank sample extract was prepared by ETL for analysis by the DFO laboratory. In addition, DFO technicians included procedural blanks that were used to assess sample preparation and analysis as well as to adjust data obtained from actual study samples.

Samples to be analysed for EDCs, phthalate esters, and nonylphenol ethoxylates were also spiked by ETL with various labeled surrogate compounds (^{13}C -NP, ^{13}C -NP1EO, ^{13}C -NP2EO, ^{13}C -NP3EO, DnOP-d4, d4-DMP, d4-DBP, and d4-DOP) and a non-labeled surrogate (polyoxyethylene-6-myristyl ether), hereafter referred to as Standard ‘A’ (StdA), prior to sample extraction. This was done to monitor extraction efficiency, evaluate procedure performance, and permit recovery correction of data from actual effluent and stream samples.

With the exception of the mono-phthalate ester samples, which were not spiked with an internal standard by ETL, target concentrations reported by the DFO laboratory were recovery corrected. Due to considerable losses of labeled surrogates ^{13}C -NP1EO and ^{13}C -NP2EO, recovery of the labeled surrogate ^{13}C -NP3EO was used to correct measured concentrations of nonylphenol ethoxylates NP1EO through NP3EO. Similarly, recovery of StdA was applied to adjust results for nonylphenol ethoxylates NP4EO through NP19EO. Concentrations of nonylphenol and those compounds analysed using the high-resolution mass spectrometer were corrected on the basis of DnOP-d4 recovery, while diphtalate esters were adjusted based on recovery of three d4-labeled surrogates (d4-DMP, d4-DBP, and d4-DOP).

3.0 RESULTS AND DISCUSSION

3.1 Quality Assurance

3.1.1 Spiked Samples

Median surrogate recovery rates for samples analysed by the DFO laboratory were somewhat variable (Appendix I). Most notably, the surrogate ^{13}C -NP1EO was not detected in any samples, while recoveries of ^{13}C -Nonylphenol and ^{13}C -NP2EO were low. To account for this, ^{13}C -NP3EO was used for recovery correction of NP1EO, NP2EO, and NP3EO. Similarly, recovery of DnOP-d4 was used in place of ^{13}C -Nonylphenol for adjustment of nonylphenol results. Median recoveries of DnOP-d4, StdA, and the phthalate ester surrogates (d4-DMP, d4-DBP, and d4-DOP), on the other hand, were generally quite reasonable. Reasons for poor recovery rates of the nonylphenol and nonylphenol ethoxylate surrogates are unclear. However, it is speculated that this might have been the result of somewhat lengthy holding times, sample overheating, or excessive vacuuming during solvent concentration. Nevertheless, results were recovery corrected by DFO wherever possible.

3.1.2 Laboratory Blanks

Analyses of laboratory blanks returned detections for an assortment of EDCs (Appendix II), phthalate esters (Appendix III), and nonylphenol ethoxylates (Appendix V). Bisphenol A, the EDC most frequently detected in blanks, and the phthalate esters are widely used in the manufacture of plastics, which tend to be prevalent in a laboratory environment. Hence, the likelihood of inadvertent sample contamination is presumably fairly high. Similarly, nonylphenol and its various ethoxylates are used in a broad range of products, including shampoos, cosmetics, paints, and cleaning agents. They also have a variety of industrial applications as surfactants, detergents, wetting agents, de-inkers, defoamers, etc. and are used in plastics manufacturing, metal processing, and so forth. Again, the probability of sample contamination in a laboratory appears to be quite high. To account for sample contamination, concentrations of compounds found in laboratory blanks were subtracted from actual sample data. Mono-phthalate esters (Appendix IV) were not detected in blanks and did not require adjustment of results.

3.2 Pharmaceuticals

With a few exceptions, standard deviations of triplicate pharmaceutical analyses were very low (Tables 7-11, in brackets). This suggests a considerable degree of precision in the analytical procedures. As might be expected from previous results reported for the United States and Ontario (Kolpin *et al.* 2002, Metcalfe *et al.* 2004), a fairly broad suite of drugs was consistently detected in WWTP effluents. Of these, nine compounds (carbamazepine, trimethoprim, sulfamethoxazole, gemfibrozil, ofloxacin, ciprofloxacin, sulfapyridine, cotinine, and pentoxifylline) were omnipresent in effluents collected throughout the Province. Interestingly, only ciprofloxacin was among the 50 most frequently prescribed medications in Canada during 2003 (IMS Health Canada 2003). Compounds measured in receiving waters downstream of WWTP outflows were either detected at much reduced concentrations, relative to effluents, or

not all. This is not surprising, considering the effects of dilution, photodegradation, and biodegradation.

3.2.1 *Acidic Pharmaceuticals*

It is important to note that the terms “acidic” and “neutral”, as used in this report, refer to the laboratory procedures used to analyse pharmaceutical compounds and, aside from providing a means of grouping the substances into convenient categories, bear little pharmacological relevance.

Of the nine acidic drugs analysed (Table 7, Figures 1, 2), only two (clofibrilic acid and ketoprofen) were not detected at least once in either effluents or river waters. Of the remaining seven, anywhere from four to seven were noted in effluents from the four WWTPs in Edmonton and Calgary. With the exception of diclofenac and naproxen, which were detected in the North Saskatchewan River downstream of Edmonton but not in effluents from either of Edmonton’s WWTPs, all of these compounds were measured in markedly reduced concentrations at downstream locations. In the case of smaller municipalities (Lethbridge, Medicine Hat, and Red Deer), only gemfibrozil was detected in effluents and at downstream sites. Interestingly, gemfibrozil was also the only acidic pharmaceutical that appeared in the South Saskatchewan River upstream of the Medicine Hat WWTP outflow. This site, although not affected by Medicine Hat effluent, is downstream of all municipalities on the Bow and Oldman Rivers. Hence, compounds detected at this location may be associated with discharges from upstream communities.

3.2.2 *Neutral Pharmaceuticals*

Six of the eight tested neutral pharmaceuticals (trimethoprim, pentoxifylline, cyclophosphamide, carbamazepine, caffeine, and cotinine) appeared in nearly all WWTP effluents (Table 8, Figure 1). Of the remaining two, fluoxetine was only detected in Capital Region and Goldbar WWTP effluents, while norfluoxetine did not appear at all. Neither of these two compounds was found in surface water samples (Table 8, Figure 2). Pentoxifylline, detected at fairly low levels in effluents from all seven WWTPs, was found only once in surface waters, appearing in the Bow River at Stier’s Ranch on January 15, 2003. Similarly, cyclophosphamide was found at very low concentrations in five of seven WWTP effluents but not in any rivers. Based on its low effluent values, it is not surprising that cyclophosphamide was not detected in surface waters. The remaining four compounds – trimethoprim, carbamazepine, caffeine, and cotinine – were consistently reported for most effluents and rivers.

3.2.3 *Quinolone Antibiotics*

Of the six quinolone antibiotics analysed, only three were detected in WWTP effluents (Table 9, Figure 1). Ciprofloxacin and ofloxacin were found in samples from all treatment plants, while norfloxacin was recorded at a fairly broad range of concentrations in effluents from all but the Lethbridge WWTP. These findings are consistent with those of Lindberg *et al.* (2005), who reported the same three quinolones from effluents of five WWTPs in Sweden.

Detections of quinolone antibiotics were rare in Alberta surface waters (Table 9, Figure 2). Ciprofloxacin was found in samples from both the North Saskatchewan and Oldman Rivers, while norfloxacin was found only in the North Saskatchewan. No other quinolones were detected in provincial rivers. This may be a reflection of the relative ease with which some of these compounds are degraded or adsorbed to particulate matter (Nowara *et al.* 1997, Cardoza *et al.* 2005).

3.2.4 Sulfonamide Antibiotics

All of the five analysed sulfonamide antibiotics, commonly known as ‘sulfa drugs’, were found in effluents from WWTPs serving Edmonton and Calgary (Table 10, Figure 1). In the case of treatment facilities in smaller municipalities, only sulfapyridine and sulfamethoxazole were detected. These same two compounds were found in the North Saskatchewan, Bow, and Oldman Rivers, downstream of their respective WWTPs (Table 10, Figure 2). The remaining three sulfonamides – sulfacetamide, sulfamethazine, and sulfisoxazole – were not detected in any surface waters. Sulfamethoxazole, the only sulfonamide noted in samples from the South Saskatchewan River upstream of Medicine Hat, also happened to be the only one of seven tested sulfonamides detected in a reconnaissance of 51 agricultural streams in the United States (Scribner *et al.* 2003). This seems reasonable, given its previously demonstrated persistence in field microcosms (Lam *et al.* 2004). None of the sulfa drugs were detected in the Red Deer River.

3.2.5 Tetracycline Antibiotics

Tetracycline antibiotics were rarely detected in WWTP effluents (Table 11, Figure 1). Tetracycline itself was only found twice, appearing in samples collected at the Gold Bar (Edmonton) WWTP and Lethbridge WWTP. The latter sample also contained doxycycline. No other tetracyclines were reported from any of the effluents, nor were any of these antibiotics detected in river water samples (Table 11, Figure 2).

3.3 Endocrine Disrupting Compounds

Thirteen of 32 EDCs were consistently detected in WWTP effluents (Table 12, Figure 3). Most of these thirteen compounds, the majority of which were plant or animal sterols, occurred at low concentrations, with very few exceeding 1 µg/L. Only nonylphenol, cholesterol, and fucosterol were found in concentrations greater than 1 µg/L in effluents from a few of the treatment plants.

Thirteen EDCs consistently appeared at measurable concentrations in most rivers (Table 13, Figure 4). Not surprisingly, twelve of these were among the thirteen detected most frequently in effluents. As expected, the vast majority of EDC detections in river water were much lower in concentration than those in corresponding effluents. An exception to this was bisphenol A, which exceeded 1.5 µg/L in the Oldman River but was considerably lower in Lethbridge WWTP effluent. Interestingly, the thirteenth compound to be regularly reported from river water samples, desmosterol, was detected in effluents from only three WWTPs but occurred at low concentrations in all five rivers.

Steroid estrogens (Table 12, in italics) were detected infrequently in WWTP effluents, with only one out of twelve compounds appearing in more than half the samples. Estrone occurred at very low concentrations in six of eight effluents, while estriol and 17 β -Estriol were each detected in four effluents. Three additional compounds – (-)-norgestrel, 17 α -ethynylestradiol, and 17 α -estradiol – were each detected only once. The remaining 5 steroid estrogens were not found in WWTP effluents. It is noteworthy that 19-norethindrone, a synthetic ovulation inhibitor not detected in effluent samples, was the only steroid estrogen detected in surface waters, appearing at low concentrations in both the North Saskatchewan and Red Deer Rivers (Table 13, Figure 4). In contrast, all the steroid estrogens included in the present survey, with the exception of β -estradiol-3-benzoate, were found in at least some of 139 receiving streams in the United States (Kolpin *et al.* 2002).

3.4 Phthalate Esters

Endocrine disrupting impacts of many phthalate esters are currently unclear. Nonetheless, several of the phthalate esters included in our study have been shown to exert estrogenic influences in various test organisms (Birkett 2003). Due to their widespread use in plastics manufacturing and their almost ubiquitous presence in the environment (Thuren and Woin 1991, McDowell and Metcalfe 2001), some phthalate esters are viewed as problem pollutants.

With the exception of two blank-corrected values that fell below detection limits, all thirteen target phthalate esters were found at measurable concentrations in effluents from all WWTPs (Table 14, Figure 5). Most occurred at values well below 1 $\mu\text{g/L}$. However, the C8-iso-mix and DEHP ranged as high as 5 $\mu\text{g/L}$ in some effluents. The C9- and C10-iso-mixes also exceeded 1 $\mu\text{g/L}$ in Gold Bar WWTP effluent, while DBP was relatively high in Capital Region WWTP effluent.

Although all of the thirteen phthalate esters examined during this project were detected in most of the receiving rivers, they were generally present at very low concentrations. Only two compounds – the C8-iso-mix and DEHP – appeared at values in excess of 1 $\mu\text{g/L}$ in two rivers. In the case of the Red Deer River, where WWTP effluent concentrations of the two phthalate esters in question were relatively high, this is consistent with expectations. However, reasons for elevated levels of C8-iso-mix and DEHP in the Oldman River are unclear, particularly since Lethbridge effluent concentrations of these two analytes were the lowest of any WWTP. Regardless, the Canadian Council of Ministers of the Environment (CCME) DEHP guideline for the protection of aquatic life (16 $\mu\text{g/L}$) was never approached during our study.

Only one of nine tested mono-phthalate esters was detected in WWTP effluents (Table 16). The M C8-iso-mix appeared at low concentrations in samples from all but the Red Deer WWTP. It was also measured at minute concentrations in all rivers but the Oldman.

3.5 Nonylphenol ethoxylates

Of the nineteen nonylphenol ethoxylates (NPEs) studied, five, NP1EO through NP5EO, were consistently detected in all effluents. However, the full suite of nineteen did appear in effluents from the Capital Region, Fish Creek, Lethbridge, and Medicine Hat WWTPs (Table 17,

Figure 7). In general, those compounds with fewer ethoxylate groups, as identified by the number in the name (e.g. NP3EO has three ethoxylate groups), occurred at the highest concentrations. This is not surprising, since these are also the most persistent of the NPEs (Ahel *et al.* 1996, Fujita *et al.* 2000). Although effluents from the Bonnybrook, Red Deer, Gold Bar, and Capital Region (replicate 1) WWTPs appeared to contain a smaller range of compounds, it should be emphasized that NPEs with longer chains of ethoxylate groups typically undergo microbially-mediated degradation to NPEs with 1-3 ethoxylate groups (Ahel *et al.* 1996). Hence, longer holding times prior to sample analysis may lead to greater concentrations of NPEs with fewer ethoxylate groups and lower concentrations of NPEs with more ethoxylate groups. This may address, for example, why NP1EO was measured at relatively high concentration in Gold Bar WWTP effluent, while NPEs greater than NP5EO were below detection limits. This may also help explain some of the differences between the two Capital Region WWTP effluent samples – the only instance in which replication took place.

After surface water data were corrected for detections in blank samples (Table 18, Figure 8), only the Bow River sample was shown to contain the full suite of nineteen NPEs. Detections in the five remaining river samples ranged from four to twelve compounds per sample, while concentrations of individual NPEs were generally quite low. Following conversion to nonylphenol equivalents and subsequent summation (Table 18), NPE concentrations in the Oldman River (1.4 µg/L) were found to exceed the CCME nonylphenol guideline value for the protection of aquatic life (1.0 µg/L; Canadian Council of Ministers of the Environment 2001).

4.0 CONCLUSION

This preliminary survey has confirmed the presence of a fairly broad range of pharmaceuticals, endocrine disruptors, and other organic wastewater contaminants in wastewater treatment plant effluents and receiving rivers of Alberta. Overall, concentrations of most of the analysed compounds were similar to those reported from other areas in Canada, the United States, and Europe (e.g. Kolpin *et al.* 2002, Metcalfe *et al.* 2004, Sacher *et al.* 1998). It must be emphasized, however, that values reported herein are the result of an initial scoping survey and should not be taken out of context. The primary purpose of this project was to establish the presence or absence of selected OWCs in effluents and surface waters of the Province. Hence, reported data are based largely on non-replicated, one-time samples and should be viewed with caution. It is also important to note that many of the studied OWCs could potentially be subject to fluctuations over time, both on a daily and seasonal basis. In addition, the possibility of long-term and cumulative environmental impacts cannot be ruled out. Therefore, having established that certain contaminants do appear with some degree of regularity throughout the Province, a more thorough, longer-term study that would help assess the risk of OWCs to the aquatic environment is warranted.

5.0 RECOMMENDATIONS

Results of this survey demonstrate that a fairly broad range of pharmaceuticals, endocrine disrupting compounds (EDCs), and other organic wastewater contaminants (OWCs) are released via wastewater treatment plant (WWTP) effluents to receiving waters in Alberta:

1. Long-term monitoring of river water upstream and downstream of major urban centres is recommended as a means of evaluating spatial and temporal trends as well as seasonal variation in OWC concentrations. Such monitoring would also permit a more thorough assessment of compounds of concern, their distribution, frequency of occurrence, and potential implications for water quality and ecosystem health in the Province.
2. Additional work on the fate and transport of pharmaceuticals, EDCs, and other OWCs in provincial surface waters is suggested. Knowledge obtained could subsequently be used to support quantitative modelling for these compounds as well as risk assessments both in terms of water quality and ecosystem health. Studies could include analyses of target OWCs in river sediments and the tissues of various aquatic organisms such as invertebrates and fishes.
3. Analyses of both WWTP influent and WWTP effluent may help evaluate treatment efficiency and could be used to compare between different treatment processes and treatment plants. Knowledge thus obtained may be used in the future to help reduce pharmaceutical, EDC, and other OWC loading to surface waters.
4. Data obtained from the above-recommended studies, in conjunction with those from other sources, should be used in the future to support the development of guidelines for pharmaceuticals, EDCs, and other OWCs in surface waters.

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7.0 TABLES

Table 1 Summary of acidic pharmaceuticals analysed in WWTP effluents and receiving rivers of Alberta. Details based on Karch (2003).

	Compound	Applications	Common Trade Names	Dosage, Comments
Acidic Pharmaceuticals	Bezafibrate	Lipid regulator	Befizal, Bezalip	200 mg two or three times daily.
	Clofibric acid	Lipid regulator (active metabolite)	Active metabolite of Clofibrate, Atromid-S, Claripex, Novofibrate	1.5-2 g two to four times daily .
	Diclofenac	Analgesic/anti-inflammatory	Apo-Dicho, Novo-Difenac, Novo-Difenac-K, Nu-Diclo, PMS-Diclofenac, Voltaren, Voltaren Ophtha, Voltaren Rapide	75-150 mg daily.
	Fenoprofen	Analgesic/anti-inflammatory	Fenopron, Nalfon	300-600 mg four times a day (200 mg oral four times a day for mild to moderate pain).
	Gemfibrozil	Lipid-regulator	Lopid, Apo-Gemfibrozil, Gen-Gemfibrozil, Novo-Gemfibrozil, Nu-Gemfibrozil, PMS-Gemfibrozil, ratio-Gemfibrozil	600 mg twice daily.
	Ibuprofen	Analgesic/anti-inflammatory	Advil, Apo-Ibuprofen, Motrin, Novo-Profen, Nu-Ibuprofen	400 mg, repeated as required every four to six hours. Maximum daily dose is 2,400 mg. Pediatric fever: 5-10 mg/kg/d oral in 3-4 divided doses, 20 mg/d for milder illness.
	Indomethacin	Analgesic/anti-inflammatory	Amuno, Apo-Indomethacin, Indocid, Indotec, Novo-Methacin, Nu-Indo, ratio-Indomethacin, Rhodacine	100-200 mg daily. Pediatric: Special circumstances, 2-4 mg/kg/d up to 150-200 mg/d.
	Ketoprofen	Analgesic/anti-inflammatory	Apo-Keto, Novo-Keto, Nu-Ketoprofen, Orudis SR, Oruvail, Rhodis, Rhovail	150-200 mg daily. Over-the-counter: 12.5 mg orally, four times daily.
	Naproxen	Analgesic/anti-inflammatory	Naprosyn, Apo-Naproxen, ratio-Naproxen, Novo-Naprox, Nu-Naprox, Gen-Naproxen EC, Apo-Naproxen EC, ratio-Naproxen E, ratio-Naproxen SR	500-1000 mg per day in divided doses. Pediatric: 10 mg/kg orally, in 2 divided doses.

Table 2 Summary of neutral pharmaceuticals analysed in WWTP effluents and receiving rivers of Alberta. Details based on Karch (2003).

	Compound	Applications	Common Trade Names	Dosage, Comments
Neutral Pharmaceuticals	Caffeine	Stimulant, marker of human waste contamination.	Cafergot (ergotamine – caffeine)	Pediatric (neonatal): 10 mg/kg intravenous followed by 2.5 mg/kg/d as maintenance. Adult: 100-200 mg orally every 3-4h, as needed. Average dosage of 184 mg caffeine (range 96-288).
	Carbamazepine	Anti-epileptic, anticonvulsant, antidiuretic, antimanic, antineuralgic, antipsychotic	Tegratal, Mazepine , Apo-Carbamazepine, Novo-Carbamaz, Nu-Carbamazepine, PMS-Carbamazepine Chewtabs, PMS-Carbamazepine CR, Taro-Carbamazepine, Tegretol	From 100-200 mg daily, up to 1,200 mg daily in divided doses. Maintenance usually 800-1200 mg/d.
	Cotinine	Metabolite of nicotine, marker of human waste contamination.		No therapeutic uses.
	Cyclophosphamide	Antineoplastic; Immunosuppressive (used in treatment of some cancers)	Cytoxan, Procytox	Recommended dose varies widely according to the specific disease being treated, the response to therapy, and other drugs being used (Induction therapy 40-50 mg/kg, intravenous in divided doses, or 1-5 mg/kg/d, maintenance 1-5 mg/kg).
	Fluoxetine	Psychiatric drug, antidepressant, antiobsessional, antilulimic	Prozac, Apo-Fluoxetine, Dom-Fluoxetine, Fluoxetine, FXT 10, FXT 20, FXT 40, Gen-Fluoxetine, Novo-Fluoxetine, Nu-Fluoxetine, PMS-Fluoxetine, ratio-Fluoxetine	20-60 mg once daily.
	Norfluoxetine	Primary metabolite of fluoxetine.		
	Pentoxifylline	Vasodilator (used to improve blood flow and treat leg pain associated with poor circulation)	Trental, Albert-Pentoxifylline, Apo-Pentoxifylline SR, Nu-Pentoxifylline SR, ratio-Pentoxifylline	400 mg twice daily.
Trimethoprim	Antibiotic, human and veterinary applications.	Proloprim, Trimpex (US)	100 mg twice daily (every 12 hours) or 200 mg once daily (every 24 hours) for a period of 10 days.	

Table 3 Summary of antibiotics analysed in WWTP effluents and receiving rivers of Alberta. Details based on Karch (2003).

	Compound	Applications	Common Trade Names	Dosage, Comments
Quinolone Antibiotics	Ciprofloxacin	Antibacterial	Ciflox, Ciproxan, Ciproxin, Cipro, Ciprobay, Velmonit	1000 mg daily. Lowest dosage for urinary tract infections, 100-250 mg orally every 12 hr for 3 days.
	Enrofloxacin	Only veterinary applications for different types of infections.	Baytril	5-20 mg/kg/day.
	Norfloxacin	Use in human medicine: urinary tract (bladder) infections.	Apo-Norflox, Noroxin, Novo-Norfloxacin, PMS-Norfloxacin	400 mg twice daily.
	Ofloxacin	Use in human medicine: infections of the lung, skin, and bladder.	Apo-Oflox, Floxin, Tarivid	300-400 mg twice daily. 200 mg twice daily for uncomplicated urinary tract infections.
	Oxolinic acid	Veterinary medicine for use in fin fish, calves, pigs and poultry .	Utibid	12 mg/kg/day. Pigs and poultry 20 mg/kg/day.
	Pipemidic acid	Antimicrobial used for gastrointestinal, biliary, and urinary infections.	Pipram	500 mg twice daily for urinary tract infections.
Sulfonamide Antibiotics	Sulfacetamide	Anti-infective (such as eye)	AK-Sulf, Bleph-10, Cetamide, Isopto Cetamide, Ocusulf-10, Sulf-10, Sulfac 10%, Sulfacet Sodium	1 drop, 4-6 times daily.
	Sulfamethazine	Greatest quantity of all sulfonamides applied in veterinary medicine; also used in human medicine. Used to treat respiratory diseases and promote accelerated weight gain in food animals.	Sulphamezathine, Sulmet	Used as cream or tablets.
	Sulfamethoxazole	Treatment of infections caused by a variety of bacteria and protozoa; often administered in combination with trimethoprim (TMP/SMX).	Gantanol, Urobak	Adults take 2 g to start, then 1 g every 8-12 hours, depending on the severity of the infection. The total daily dosage should not exceed 3 g.
	Sulfapyridine	Used to control dermatitis herpetiformis (Duhring's disease), etc.	Dagenan	250-1000 mg four times daily until improvement.
	Sulfisoxazole	Eliminates bacteria that cause infections, especially urinary tract and ear infections.	Gantrisin, Apo-Sulfisoxazole, Novo-Soxazole, Sulfizole	Adult: 2-8 g daily in 4-6 doses. Pediatric: 75-150 mg/kg/day in 4-6 divided doses. Sexually transmitted disease: 500 mg/d for 21 d.
Tetracycline Antibiotics	Chlorotetracycline	Mainly used as growth promoter for chicken, swine, and turkey.	Aureomycin, Achromycin	5.5 mg/kg (0.00055%) of complete feed.
	Doxycycline	Used to treat lung, urinary tract, throat, and skin infections.	Nordox, Apo-Doxy, Doxycin, Novo-Doxylin, Nu-Doxycycline, ratio-Doxycycline, Vibra-Tabs	200 mg for the first dose, followed by 100 mg once daily.
	Oxytetracycline	Mainly as growth promoter for livestock.	Terramycin	
	Tetracycline	Used to treat infections of the skin and Lyme disease. Also used in combination with other compounds for treatment of the bacterium (<i>Helicobacter pylori</i>) that causes ulcers.	Tetra-Sol, Apo-Tetra, Novo-Tetra, Nu-Tetra	250-500 mg four times daily.

Table 4 Summary of endocrine disrupting compounds analysed in WWTP effluents and receiving rivers of Alberta.

	Target Analyte	Description and/or Full Name
Endocrine Disrupting Compounds (EDCs)	Nonylphenol	Potent EDC from surfactants, formulant in pesticides, lubricating oil additive, curing of epoxy resins
	Cholesterol	Animal derived sterol
	Fucosterol	Sterol found in seaweed
	Stigmasterol	Major wood derived sterol
	Campesterol	Major wood derived sterol
	β -Sitosterol	Major wood derived sterol
	Coprostan-3-one	Fecal neutral sterol
	Cholestanol (Coprostanol)	Cholesterol derivative
	Stigmastanol	Major wood derived sterol
	Bisphenol A	Potent EDC from PVC plastics
	7-Ketocholesterol	Cholesterol oxidation product
	Desmosterol	Cholesterol derivative
	Kaempferol	Flavonoid found in woody plants
	6-Ketocholestanol	Cholesterol oxidation product
	Genistein	Flavonoid found in soy products and pulp mill effluents
	Totarol	Antibacterial diterpenoid
	Pinosylvin	Stilbene found in <i>Pinus</i> species
	α -Zearalanol	Veterinary drug - growth promoter
	Naringenin	Flavonoid found in woody plants
	Ergosterol	Main sterol produced by fungi
	Estrone	Endogenous female estrogen
	(-)-Norgestrel	Synthetic ovulation inhibitor (birth control pill)
	17 α -Ethinylestradiol	Synthetic ovulation inhibitor (birth control pill)
	Estriol	Endogenous female estrogen
	17 β -Estradiol	Endogenous female estrogen
	17 α -Estradiol	Endogenous female estrogen
	Equilin	Hormone replacement therapy drug
	Testosterone	Endogenous male androgen
	d-Equilenin	Hormone replacement therapy drug
	Mestranol	Synthetic ovulation inhibitor (birth control pill)
	19-Norethindrone	Synthetic ovulation inhibitor (birth control pill)
β -Estradiol-3-benzoate	Veterinary drug - growth promoter	

Table 5 Summary of phthalate esters, mono-phthalate, and nonylphenol ethoxylates analysed in WWTP effluents and receiving rivers of Alberta.

	Target Analyte	Description and/or Full Name
Phthalate Esters	Dimethyl phthalate - DMP	Used as a rubber softener and in wood stains and varnishes
	Diethyl phthalate - DEP	Used as a plasticizer and in cosmetics, insecticides, and aspirin
	Diisobutyl phthalate - DIBP	Solvent, PVC production, synthetic rubber manufacture
	Di-n-butyl phthalate - DBP	PVC and nitrocellulose lacquers - carpets, paints, insect repellents, hair spray
	Butylbenzyl phthalate - BBP	PVC and nitrocellulose resin. Used to coat electrical wires
	Di(2-ethylhexyl) phthalate - DEHP	Very commonly used plasticizer in a broad range of consumer products
	Di-n-octyl phthalate - DnOP	Plasticizer, pesticide
	Dinonyl phthalate - DNP	Film and sheeting, extruded and molded automotive applications
	C6-iso-mix	
	C7-iso-mix	
	C8-iso-mix**	DEHP + DnOP and reported from GC/MS analysis of individual DEHP and DnOP
	C9-iso-mix	
	C10-iso-mix	
	d-4 dimethyl phthalate - d-4 DMP	
	d-4 di-n-butyl phthalate - d-4 DBP	
d-4 di-n-octyl phthalate - d-4 DOP		
Mono-phthalate Esters	Monomethyl phthalate - MMP	Dimethyl phthalate metabolite.
	Monoethyl phthalate - MEP	Diethyl phthalate metabolite.
	Monobutyl phthalate - MButP	Dibutyl phthalate metabolite.
	M C6-iso-mix	
	Monobenzyl phthalate - MBzP	Butylbenzyl phthalate metabolite.
	M C7-iso-mix	
	MEHP+MnOP (M C8-iso mix)	
	M C9-iso-mix	
	M-C10-iso-mix	
	MBuP - C13	Mono-n-butyl phthalate-ring-1,2-13C-dicarboxyl-13-C2
MEHP - C13	Mono-2-ethylhexyl phthalate-ring-1,2-13C-dicarboxyl-13-C2	
Nonylphenol Ethoxylates	NP1EO	These compounds are widely used in household laundry detergents, shampoos, cosmetics, household cleaners, latex paint, and spermicides; industrial surfactants, detergents, wetting agents, dispersants, defoamers, de-inkers, and antistatic agents.
	NP2EO	
	NP3EO	
	NP4EO	
	NP5EO	
	NP6EO	
	NP7EO	
	NP8EO	
	NP9EO	
	NP10EO	
	NP11EO	
	NP12EO	
	NP13EO	
	NP14EO	
	NP15EO	
	NP16EO	
	NP17EO	
	NP18EO	
	NP19EO	

Table 6 Summary of wastewater treatment plants (WWTPs) and river stations sampled.

River	Municipality	WWTP	Sampling Date	WWTPs		River Station	Sampling Date	River Stations		Stream Flow (m ³ /s)
				Latitude	Longitude			Latitude	Longitude	
Bow	Calgary	Bonnybrook	15/01/2003	51° 00' 50"	114° 00' 30"	At Stier's Ranch, Downstream of Effluent	15/01/2003 **	50° 51' 18"	113° 56' 00"	78.0
		Fish Creek	15/01/2003 *	50° 54' 39"	114° 00' 30"					
North Saskatchewan	Edmonton	Capital Region	17/12/2002	53° 38' 28"	113° 18' 11"	At Fort Saskatchewan Bridge, Downstream of Effluent	17/12/2002	53° 42' 24"	113° 14' 05"	115.0
		Gold Bar	17/12/2002	53° 33' 00"	113° 28' 00"					
Oldman	Lethbridge	Lethbridge	29/01/2003	49° 43' 11"	112° 51' 42"	Southwest of Diamond City, Downstream of Effluent	29/01/2003	49° 46' 49"	112° 50' 30"	20.2
Red Deer	Red Deer	Red Deer	22/01/2003	52° 18' 52"	113° 47' 21"	At Red Deer, Downstream of Effluent	22/01/2003 †	52° 16' 35"	113° 48' 45"	15.8
South Saskatchewan	Medicine Hat	Medicine Hat	23/01/2003	50° 03' 20"	110° 38' 30"	Upstream of Medicine Hat, Upstream of Effluent	23/01/2003	50° 06' 00"	110° 39' 00"	64.6

Notes: * Resampled 12/06/2003

** Resampled 19/08/2003

† Resampled 25/08/2003

Table 7 Acidic pharmaceutical concentrations in WWTP effluents and receiving rivers of Alberta (µg/L). Bracketed values indicate standard deviation of triplicate measurements. ND = Not Detected.

		NORTH SASKATCHEWAN RIVER		BOW RIVER		OLDMAN RIVER	SOUTH SASKATCHEWAN RIVER	RED DEER RIVER	
Compound		Capital Region WWTP 17/12/02	Gold Bar WWTP 17/12/02	Fish Creek WWTP 15/01/03	Bonnybrook WWTP 15/01/03	Lethbridge WWTP 29/01/03	Medicine Hat WWTP 23/01/03	Red Deer WWTP 22/01/03	
Acidic Pharmaceuticals	Effluent	Bezafibrate	0.117 (0.021)	0.547 (0.061)	0.289 (0.020)	0.144 (0.063)	ND	ND	ND
		Clofibric acid	ND	ND	ND	ND	ND	ND	ND
		Diclofenac	ND	ND	0.429 (0.038)	0.359 (0.132)	ND	ND	ND
		Fenoprofen	0.106 (0.023)	0.355 (0.027)	0.078 (0.015)	ND	ND	ND	ND
		Gemfibrozil	0.619 (0.018)	0.652 (0.028)	0.773 (0.005)	0.799 (0.028)	0.410 (0.026)	0.606 (0.064)	0.813 (0.034)
		Ibuprofen	1.759 (0.030)	1.333 (0.124)	1.149 (0.024)	0.383 (0.094)	ND	ND	ND
		Indomethacin	0.803 (0.032)	ND	0.166 (0.014)	0.105 (0.024)	ND	ND	ND
		Ketoprofen	ND	ND	ND	ND	ND	ND	ND
		Naproxen	ND	ND	2.668 (0.016)	1.785 (0.109)	ND	ND	ND
	Receiving River	Compound	At Fort Saskatchewan Bridge (downstream of effluents) 17/12/02	At Stiers Ranch (downstream of effluents) 19/08/03		SW of Diamond City (downstream of effluent) 29/01/03	Upstream of Medicine Hat (upstream of effluent) 23/01/03	At Red Deer (downstream of effluent) 25/08/03	
			Bezafibrate	0.029 (0.005)	0.010 (0.001)		ND	ND	ND
			Clofibric acid	ND	ND		ND	ND	ND
			Diclofenac	0.090 (0.027)	0.021 (0.001)		ND	ND	ND
			Fenoprofen	0.026 (0.008)	ND		ND	ND	ND
			Gemfibrozil	0.052 (0.003)	0.023 (0.001)		0.017 (0.002)	0.067 (0.004)	0.004 (0.000)
			Ibuprofen	0.269 (0.006)	0.023 (0.002)		ND	ND	ND
			Indomethacin	0.027 (0.013)	0.020 (0.001)		ND	ND	ND
Ketoprofen			ND	ND		ND	ND	ND	
Naproxen	0.106 (0.022)	0.059 (0.002)		ND	ND	ND			

Table 8 Neutral pharmaceutical concentrations in WWTP effluents and receiving rivers of Alberta ($\mu\text{g/L}$). Bracketed values indicate standard deviation of triplicate measurements. ND = Not Detected.

		NORTH SASKATCHEWAN RIVER		BOW RIVER		OLDMAN RIVER	SOUTH SASKATCHEWAN RIVER	RED DEER RIVER	
		Capital Region WWTP 17/12/02	Gold Bar WWTP 17/12/02	Fish Creek WWTP 15/01/03	Bonnybrook WWTP 15/01/03	Lethbridge WWTP 29/01/03	Medicine Hat WWTP 23/01/03	Red Deer WWTP 22/01/03	
Neutral Pharmaceuticals	Effluent	Fluoxetine	0.031 (0.035)	0.799 (0.045)	ND	ND	ND	ND	ND
		Norfluoxetine	ND	ND	ND	ND	ND	ND	ND
		Trimethoprim	3.528 (0.404)	0.669 (0.063)	0.795 (0.041)	0.907 (0.036)	0.887 (0.057)	0.514 (0.029)	1.404 (0.024)
		Pentoxifylline	0.163 (0.004)	0.098 (0.004)	0.171 (0.006)	0.099 (0.003)	0.023 (0.005)	0.084 (0.002)	0.036 (0.001)
		Cyclophosphamide	ND	0.005 (0.002)	0.048 (0.005)	0.055 (0.001)	0.012 (0.001)	0.012 (0.001)	ND
		Carbamazepine	2.641 (0.113)	1.784 (0.035)	0.702 (0.012)	0.925 (0.031)	2.785 (0.060)	1.123 (0.029)	3.287 (0.141)
		Caffeine	ND	0.129 (0.031)	0.670 (0.051)	0.405 (0.082)	0.074 (0.017)	0.872 (0.040)	0.095 (0.008)
		Cotinine	0.162 (0.011)	0.156 (0.001)	3.476 (0.051)	0.165 (0.007)	0.030 (0.005)	0.141 (0.023)	0.131 (0.028)
		Compound	At Fort Saskatchewan Bridge (downstream of effluents) 17/12/02		At Stiers Ranch (downstream of effluents) 19/08/03		SW of Diamond City (downstream of effluent) 29/01/03	Upstream of Medicine Hat (upstream of effluent) 23/01/03	At Red Deer (downstream of effluent) 25/08/03
	Receiving River	Fluoxetine	ND		ND		ND	ND	ND
		Norfluoxetine	ND		ND		ND	ND	ND
		Trimethoprim	0.104 (0.004)		0.018 (0.002)		0.039 (0.009)	0.076 (0.008)	ND
		Pentoxifylline	ND		0.015 (0.001)		ND	ND	ND
		Cyclophosphamide	ND		ND		ND	ND	ND
		Carbamazepine	0.171 (0.003)		0.094 (0.001)		0.139 (0.001)	0.206 (0.016)	0.095 (0.005)
Caffeine		0.023 (0.006)		0.064 (0.004)		0.072 (0.004)	0.466 (0.040)	0.054 (0.002)	
Cotinine		0.009 (0.008)		0.007 (0.004)		ND	0.189 (0.003)	ND	

Table 9 Quinolone antibiotic concentrations in WWTP effluents and receiving rivers of Alberta ($\mu\text{g/L}$). Bracketed values indicate standard deviation of triplicate measurements. ND = Not Detected.

		NORTH SASKATCHEWAN RIVER		BOW RIVER		OLDMAN RIVER	SOUTH SASKATCHEWAN RIVER	RED DEER RIVER	
Compound		Capital Region WWTP 17/12/02	Gold Bar WWTP 17/12/02	Fish Creek WWTP 15/01/03	Bonnybrook WWTP 15/01/03	Lethbridge WWTP 29/01/03	Medicine Hat WWTP 23/01/03	Red Deer WWTP 22/01/03	
Quinolone Antibiotics	Effluent	Ciprofloxacin	0.651 (0.032)	0.383 (0.014)	0.556 (0.008)	0.634 (0.028)	0.207 (0.016)	0.343 (0.072)	0.888
		Enrofloxacin	ND	ND	ND	ND	ND	ND	ND
		Norfloxacin	0.096 (0.025)	0.078 (0.004)	0.492 (0.005)	0.093 (0.023)	ND	0.821 (0.100)	0.322
		Ofloxacin	0.342 (0.029)	0.182 (0.005)	0.649 (0.016)	0.341 (0.025)	0.968 (0.110)	0.634 (0.066)	0.567
		Oxolinic acid	ND	ND	ND	ND	ND	ND	ND
		Pipemidic acid	ND	ND	ND	ND	ND	ND	ND
		Compound	At Fort Saskatchewan Bridge (downstream of effluents) 17/12/02		At Stiers Ranch (downstream of effluents) 19/08/03		SW of Diamond City (downstream of effluent) 29/01/03	Upstream of Medicine Hat (upstream of effluent) 23/01/03	At Red Deer (downstream of effluent) 25/08/03
	Receiving River	Ciprofloxacin	0.081 (0.011)		ND		0.114 (0.002)	ND	ND
		Enrofloxacin	ND		ND		ND	ND	ND
		Norfloxacin	0.107 (0.007)		ND		ND	ND	ND
		Ofloxacin	ND		ND		ND	ND	ND
		Oxolinic acid	ND		ND		ND	ND	ND
		Pipemidic acid	ND		ND		ND	ND	ND

Table 10 Sulfonamide antibiotic concentrations in WWTP effluents and receiving rivers of Alberta (µg/L). Bracketed values indicate standard deviation of triplicate measurements. ND = Not Detected.

		NORTH SASKATCHEWAN RIVER		BOW RIVER		OLDMAN RIVER	SOUTH SASKATCHEWAN RIVER	RED DEER RIVER	
		Capital Region WWTP 17/12/02	Gold Bar WWTP 17/12/02	Fish Creek WWTP 15/01/03	Bonnybrook WWTP 15/01/03	Lethbridge WWTP 29/01/03	Medicine Hat WWTP 23/01/03	Red Deer WWTP 22/01/03	
Sulfonamide Antibiotics	Effluent	Sulfapyridine	0.707 (0.016)	0.182 (0.035)	0.223 (0.022)	0.323 (0.017)	0.167 (0.010)	0.297 (0.139)	0.117
		Sulfamethoxazole	3.278 (0.127)	1.020 (0.180)	0.415 (0.042)	0.931 (0.022)	0.886 (0.034)	0.363 (0.173)	0.193
		Sulfacetamide	0.105 (0.006)	0.044 (0.008)	ND	0.068 (0.001)	ND	ND	ND
		Sulfamethazine	0.023 (0.002)	ND	ND	0.072 (0.002)	ND	ND	ND
		Sulfisoxazole	0.010 (0.006)	ND	0.052 (0.007)	0.076 (0.002)	ND	ND	ND
	Receiving River	Compound	At Fort Saskatchewan Bridge (downstream of effluents) 17/12/02		At Stiers Ranch (downstream of effluents) 19/08/03		SW of Diamond City (downstream of effluent) 29/01/03	Upstream of Medicine Hat (upstream of effluent) 23/01/03	At Red Deer (downstream of effluent) 25/08/03
		Sulfapyridine	0.035 (0.004)		0.015 (0.002)		0.061 (0.000)	ND	ND
		Sulfamethoxazole	0.286 (0.007)		0.048 (0.005)		0.101 (0.010)	0.025 (0.026)	ND
		Sulfacetamide	ND		ND		ND	ND	ND
		Sulfamethazine	ND		ND		ND	ND	ND
Sulfisoxazole	ND		ND		ND	ND	ND		

Table 11 Tetracycline antibiotic concentrations in WWTP effluents and receiving rivers of Alberta (µg/L). Bracketed values indicate standard deviation of triplicate measurements. ND = Not Detected.

		NORTH SASKATCHEWAN RIVER		BOW RIVER		OLDMAN RIVER	SOUTH SASKATCHEWAN RIVER	RED DEER RIVER	
		Capital Region WWTP 17/12/02	Gold Bar WWTP 17/12/02	Fish Creek WWTP 15/01/03	Bonnybrook WWTP 15/01/03	Lethbridge WWTP 29/01/03	Medicine Hat WWTP 23/01/03	Red Deer WWTP 22/01/03	
Tetracycline Aantibiotics	Effluent	Chlorotetracycline	ND	ND	ND	ND	ND	ND	
		Doxycycline	ND	ND	ND	ND	0.102 (0.019)	ND	ND
		Oxytetracycline	ND	ND	ND	ND	ND	ND	ND
		Tetracycline	ND	0.203 (0.050)	ND	ND	0.320 (0.087)	ND	0.081
		Compound	At Fort Saskatchewan Bridge (downstream of effluents) 17/12/02		At Stiers Ranch (downstream of effluents) 19/08/03		SW of Diamond City (downstream of effluent) 29/01/03	Upstream of Medicine Hat (upstream of effluent) 23/01/03	At Red Deer (downstream of effluent) 25/08/03
	Receiving River	Chlorotetracycline	ND	ND	ND	ND	ND	ND	ND
		Doxycycline	ND	ND	ND	ND	ND	ND	ND
		Oxytetracycline	ND	ND	ND	ND	ND	ND	ND
		Tetracycline	ND	ND	ND	ND	ND	ND	ND

Table 12 EDC concentrations in WWTP effluents of Alberta (ng/L). Steroid estrogens are indicated in italics. ND = Not Detected.

Target Analyte	NORTH SASKATCHEWAN RIVER						BOW RIVER				OLDMAN RIVER		SOUTH SASKATCHEWAN RIVER		RED DEER RIVER	
	Capital Region 17/12/02		Capital Region (2) 17/12/02		Gold Bar 17/12/02		Fish Creek 12/6/03		Bonnybrook 15/01/03		Lethbridge 29/01/03		Medicine Hat 23/01/03		Red Deer 22/01/03	
	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected
Nonylphenol	0.00	ND	226.60	178.72	2439.79	2391.92	ND	ND	1787.87	1733.51	206.08	184.54	2809.72	2771.77	834.21	786.33
Cholesterol	800.59	800.59	337.47	337.47	290.11	290.11	2143.84	2140.14	413.65	413.65	86.00	85.34	1570.79	1570.46	672.45	672.45
Fucosterol	681.23	681.23	372.72	372.72	847.10	847.10	1798.32	1798.32	577.54	577.54	53.04	53.04	870.11	870.11	523.79	523.79
Stigmasterol	425.37	425.37	96.49	96.49	363.02	363.02	626.32	626.32	177.14	177.14	9.74	9.74	284.05	284.05	180.39	180.39
Campesterol	342.01	342.01	135.09	135.09	233.21	233.21	ND	ND	153.24	153.24	6.58	6.58	764.88	764.88	177.24	177.24
<i>β</i> -Sitosterol	331.10	330.83	227.14	226.86	367.67	367.39	751.12	751.12	202.85	202.85	32.33	32.33	397.49	397.49	209.60	209.33
Coprostan-3-one	314.05	313.76	88.97	88.67	181.45	181.15	ND	ND	155.08	154.49	27.92	27.92	402.28	401.98	171.74	171.45
Cholestanol (Coprostanol)	136.59	136.59	51.23	51.23	121.97	121.97	810.53	810.53	132.30	132.30	6.21	6.21	271.65	271.65	107.07	107.07
Stigmastanol	87.67	87.67	20.92	20.92	44.29	44.29	330.04	330.04	29.81	29.81	4.83	4.83	108.34	108.34	35.84	35.84
Bisphenol A	29.85	6.49	21.15	ND	139.29	115.93	195.12	194.55	125.34	83.57	1.95	1.29	58.15	36.93	49.71	26.34
7-Ketocholesterol	83.73	83.73	126.29	126.29	40.81	40.81	130.72	130.72	14.82	14.82	52.37	52.37	74.73	74.73	36.21	36.21
Desmosterol	ND	ND	102.28	102.28	ND	ND	ND	ND	ND	ND	68.49	68.49	ND	ND	143.74	143.74
Kaempferol	ND	ND	ND	ND	56.43	56.43	13.45	13.45	ND	ND	0.00	ND	40.79	40.79	48.29	48.29
6-Ketocholestanol	18.00	18.00	7.82	7.82	ND	ND	20.69	20.69	ND	ND	4.57	4.57	16.20	16.20	9.65	9.65
Genistein	ND	ND	ND	ND	9.89	9.89	ND	ND	ND	ND	0.00	ND	ND	ND	ND	ND
Totanol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	3.11	3.11	ND	ND
Pinosylvin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	1.49	1.49	ND	ND
<i>α</i> -Zearalanol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND	ND	ND
Naringenin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND	ND	ND
Ergosterol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND	ND	ND
<i>Estrone</i>	3.34	3.34	0.26	0.26	34.06	34.06	ND	ND	2.56	2.56	0.00	ND	10.27	10.27	9.93	9.93
<i>(-)-Norgestrel</i>	22.23	22.23	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND	ND	ND
<i>17α-Ethinylestradiol</i>	ND	ND	ND	ND	ND	ND	8.47	8.47	ND	ND	0.00	ND	ND	ND	ND	ND
<i>Estriol</i>	ND	ND	ND	ND	3.43	3.43	ND	ND	3.99	3.99	0.00	ND	2.51	2.51	2.19	2.19
<i>17β-Estradiol</i>	ND	ND	ND	ND	2.08	2.08	ND	ND	1.48	1.48	0.21	0.21	2.73	2.73	ND	ND
<i>17α-Estradiol</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	1.79	1.79	ND	ND
<i>Equilin</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND	ND	ND
<i>Testosterone</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND	ND	ND
<i>d-Equilenin</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND	ND	ND
<i>Mestranol</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND	ND	ND
<i>19-Norethindrone</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND	ND	ND
<i>β-Estradiol-3-benzoate</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND	ND	ND
Surrogate (% Recovery)																
¹³ C-Nonylphenol	0.09%		0.35%		0.95%		ND		0.58%		0.14%		0.39%		0.92%	
DnOP-d4	86.80%		11.94%		45.70%		50.90%		33.50%		28.30%		74.60%		71.60%	

Table 13 EDC concentrations in receiving rivers of Alberta (ng/L). Steroid estrogens are indicated in italics. ND = Not Detected.

Target Analyte	North Saskatchewan River at Ft. Saskatchewan Bridge (downstream of effluents) 17/12/02		Bow River at Stiers Ranch (downstream of effluents) 15/01/03		Oldman River SW of Diamond City (downstream of effluent) 29/01/03		South Saskatchewan River Upstream of Medicine Hat (upstream of effluent) 23/01/03		Red Deer River at Red Deer (downstream of effluent) 22/01/03	
	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected
Nonylphenol	30.98	ND	313.81	292.27	223.50	175.62	157.16	119.22	84.07	36.19
Cholesterol	69.96	69.96	285.75	285.10	224.87	224.87	216.61	216.28	64.53	64.53
Fucosterol	113.69	113.69	135.87	135.87	957.40	957.40	136.75	136.75	ND	ND
Stigmasterol	12.65	12.65	ND	ND	252.42	252.42	44.61	44.61	21.09	21.09
Campesterol	12.99	12.99	19.98	19.98	193.55	193.55	36.78	36.78	10.59	10.59
<i>β</i> -Sitosterol	59.85	59.58	73.28	73.28	579.80	579.52	84.22	84.22	52.33	52.05
Coprostan-3-one	9.00	8.70	17.65	17.65	ND	ND	26.38	26.08	17.03	16.73
Cholestanol (Coprostanol)	2.47	2.47	10.01	10.01	12.37	12.37	20.55	20.55	6.45	6.45
Stigmastanol	2.77	2.77	8.73	8.73	47.83	47.83	9.88	9.88	4.41	4.41
Bisphenol A	3.01	ND	2.46	1.80	1550.72	1527.35	7.13	ND	65.92	42.55
7-Ketocholesterol	5.92	5.92	105.98	105.98	80.49	80.49	45.59	45.59	47.44	47.44
Desmosterol	11.40	11.40	165.23	165.23	94.93	94.93	61.30	61.30	65.60	65.60
Kaempferol	ND	ND	2.84	2.84	ND	ND	ND	ND	ND	ND
6-Ketocholestanol	0.65	0.65	7.39	7.39	18.46	18.46	7.85	7.85	4.85	4.85
Genistein	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Totanol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pinosylvin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>α</i> -Zearalanol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Naringenin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ergosterol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>Estrone</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>(-)-Norgestrel</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>17α-Ethinylestradiol</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>Estriol</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>17β-Estradiol</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>17α-Estradiol</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>Equilin</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>Testosterone</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>α-Equilenin</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>Mestranol</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>19-Norethindrone</i>	0.58	0.58	ND	ND	ND	ND	ND	ND	ND	0.77
<i>β-Estradiol-3-benzoate</i>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Surrogate (% Recovery)										
¹³ C-Nonylphenol	0.35%		0.08%		0.04%		0.00		0.50%	
DnOP-d4	88.80%		44.38%		1.50%		0.75		102.20%	

Table 14 Phthalate ester concentrations in WWTP effluents of Alberta (ng/L). ND = Not Detected.

Target Analyte	NORTH SASKATCHEWAN RIVER						BOW RIVER				OLDMAN RIVER		SOUTH SASKATCHEWAN RIVER		RED DEER RIVER	
	Capital Region 17/12/02		Capital Region (2) 17/12/02		Gold Bar 17/12/02		Fish Creek 12/6/03		Bonnybrook 15/01/03		Lethbridge 29/01/03		Medicine Hat 23/01/03		Red Deer 22/01/03	
	Concentration (ng/L)	Blank Corrected (ng/L)	Concentration (ng/L)	Blank Corrected (ng/L)	Concentration (ng/L)	Blank Corrected (ng/L)	Concentration (ng/L)	Blank Corrected (ng/L)	Concentration (ng/L)	Blank Corrected (ng/L)	Concentration (ng/L)	Blank Corrected (ng/L)	Concentration (ng/L)	Blank Corrected (ng/L)	Concentration (ng/L)	Blank Corrected (ng/L)
C6-iso-mix	43.9	43.9	24.2	24.2	141.9	141.9	5.8	5.8	0.0	ND	1.0	1.0	37.0	37.0	9.2	9.2
C7-iso-mix	194.2	194.2	57.9	57.9	121.9	121.9	88.1	88.1	43.8	43.8	49.7	49.7	110.5	110.5	43.9	43.9
C8-iso-mix	2671.3	2666.6	1139.2	1134.5	4793.8	4772.6	5225.4	5211.4	396.7	392.0	126.9	105.7	3052.8	3048.1	5513.5	5508.8
C9-iso-mix	762.4	762.4	115.5	115.5	1107.9	1107.9	373.8	373.8	30.0	30.0	38.2	38.2	180.5	180.5	147.6	147.6
C10-iso-mix	680.1	680.1	105.2	105.2	1295.8	1295.8	243.7	243.7	35.8	35.8	21.8	21.8	170.2	170.2	64.5	64.5
DEHP	2650.4	2645.9	1133.3	1128.8	4761.6	4741.6	5195.8	5182.1	394.8	390.3	125.5	105.5	3041.5	3037.0	5505.0	5500.5
DBP	1421.5	1385.4	86.8	50.6	123.5	57.2	269.7	246.8	137.3	101.2	82.4	16.1	63.0	26.9	87.8	51.6
DEP	105.7	95.1	12.2	1.6	17.7	14.4	217.5	213.4	33.5	22.9	11.3	8.0	28.3	17.7	30.6	20.0
DNP	85.0	85.0	23.7	23.7	46.7	46.0	130.1	130.1	3.6	3.6	3.9	3.2	31.5	31.5	17.7	17.7
DIBP	62.2	56.2	60.3	54.3	11.3	6.4	108.3	107.0	16.7	10.7	6.6	1.7	30.6	24.6	13.5	7.5
BBP	38.4	36.3	17.8	15.6	14.2	3.5	82.8	77.7	10.1	8.0	9.4	ND	16.5	14.3	18.3	16.2
DnOP	20.9	20.7	5.9	5.7	32.2	31.1	29.6	29.2	1.9	1.8	1.4	0.3	11.3	11.1	8.5	8.4
DMP	1.9	1.1	0.8	0.0	1.2	1.0	4.1	3.9	2.2	1.4	0.4	0.3	0.8	ND	0.9	0.1
Surrogate (% Recovery)																
d4-DMP	43.7%		65.2%		23.3%		21.3%		21.1%		NA		54.3%		49.9%	
d4-DBP	61.1%		68.2%		59.7%		86.9%		67.4%		NA		80.2%		68.5%	
d4-DOP	48.5%		88.6%		62.8%		84.1%		78.9%		NA		87.3%		86.3%	

Table 15 Phthalate ester concentrations in receiving rivers of Alberta (ng/L). ND = Not Detected.

Target Analyte	North Saskatchewan River at Ft. Saskatchewan Bridge (downstream of effluents) 17/12/02		Bow River at Stiers Ranch (downstream of effluents) 15/01/03		Oldman River SW of Diamond City (downstream of effluent) 29/01/03		South Saskatchewan River Upstream of Medicine Hat (upstream of effluent) 23/01/03		Red Deer River at Red Deer (downstream of effluent) 22/01/03	
	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected
C6-iso-mix	3.4	3.4	27.2	27.2	0.0	ND	3.9	3.9	0.0	ND
C7-iso-mix	17.9	17.9	158.4	158.4	51.8	51.8	68.7	68.7	53.6	53.6
C8-iso-mix	81.1	76.4	709.3	688.1	2063.4	2058.7	766.9	762.2	1723.2	1718.5
C9-iso-mix	18.3	18.3	176.8	176.8	18.2	18.2	66.0	66.0	245.9	245.9
C10-iso-mix	41.9	41.9	128.4	128.4	26.9	26.9	43.1	43.1	33.1	33.1
DEHP	80.1	75.5	704.1	684.1	2060.3	2055.8	763.3	758.8	1719.5	1715.0
DBP	41.9	5.8	235.7	169.4	77.2	41.0	124.0	87.8	35.9	ND
DEP	29.1	18.5	51.8	48.5	33.2	22.6	13.3	2.7	19.8	9.2
DNP	3.8	3.8	20.7	20.0	5.6	5.6	12.5	12.5	12.5	12.5
DIBP	2.0	ND	13.9	9.0	5.1	ND	5.9	ND	5.4	ND
BBP	3.3	1.2	32.4	21.7	10.3	8.2	9.1	6.9	18.2	16.1
DnOP	1.0	0.8	5.2	4.0	3.1	2.9	3.6	3.4	3.7	3.5
DMP	0.4	ND	3.4	3.2	1.6	0.8	1.1	0.3	1.0	0.2
Surrogate (% Recovery)										
d4-DMP	31.5%		38.5%		5.2%		54.6%		10.3%	
d4-DBP	86.9%		75.6%		32.4%		79.2%		73.6%	
d4-DOP	74.4%		65.1%		30.3%		74.9%		79.2%	

Table 16 Mono-phthalate ester concentrations in WWTP effluents and receiving rivers of Alberta (ng/L). ND = Not Detected; NA = Not Analysed.

	Target Analyte	NORTH SASKATCHEWAN RIVER		BOW RIVER		OLDMAN RIVER	SOUTH SASKATCHEWAN RIVER	RED DEER RIVER	
		Capital Region WWTP 17/12/02	Gold Bar WWTP 17/12/02	Fish Creek WWTP 12/6/03	Bonnybrook WWTP 15/01/03	Lethbridge WWTP 29/01/03	Medicine Hat WWTP 23/01/03	Red Deer WWTP 22/01/03	
Mono-Phthalate Esters	Effluent (WWTPs)	MMP	ND	ND	ND	ND	ND	ND	
		MEP	ND	ND	ND	ND	ND	ND	
		MButP	ND	ND	ND	ND	ND	ND	
		M C6-iso-mix	ND	ND	ND	ND	ND	ND	
		MBzP	ND	ND	ND	ND	ND	ND	
		M C7-iso-mix	ND	ND	ND	ND	ND	ND	
		M C8-iso mix (MEHP+MnOP)	12.8	8.7	135.8	11.7	7.3	35.8	ND
		M C9-iso-mix	ND	ND	ND	ND	ND	ND	ND
		M-C10-iso-mix	ND	ND	ND	ND	ND	ND	ND
	Receiving River	Target Analyte	At Ft. Saskatchewan Bridge (downstream of effluents) 17/12/02		At Stiers Ranch (downstream of effluents) 15/01/03		SW of Diamond City (downstream of effluent) 29/01/03	Upstream of Medicine Hat (upstream of effluent) 23/01/03	At Red Deer (downstream of effluent) 22/01/03
		MMP	ND		ND		NA	ND	ND
		MEP	ND		ND		NA	ND	ND
		MButP	ND		ND		NA	ND	ND
		M C6-iso-mix	ND		ND		NA	ND	ND
		MBzP	ND		ND		NA	ND	ND
		M C7-iso-mix	ND		ND		NA	ND	ND
		M C8-iso mix (MEHP+MnOP)	1.2		5.8		NA	6.7	4.3
M C9-iso-mix	ND		ND		NA	ND	ND		
M-C10-iso-mix	ND		ND		NA	ND	ND		

Table 17 Nonylphenol ethoxylate concentrations in WWTP effluents of Alberta (ng/L). ND = Not Detected.

Target Analyte	NORTH SASKATCHEWAN RIVER						BOW RIVER				OLDMAN RIVER		SOUTH SASKATCHEWAN RIVER		RED DEER RIVER	
	Capital Region 17/12/02		Capital Region (2) 17/12/02		Gold Bar 17/12/02		Fish Creek 12/6/03		Bonnybrook 15/01/03		Lethbridge 29/01/03		Medicine Hat 23/01/03		Red Deer 22/01/03	
	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected
NP1EO	1192.63	1192.63	1193.34	1193.34	12299.03	12299.03	6099.26	6099.26	3442.72	3442.72	216.07	216.07	21951.73	21951.73	3742.82	3742.82
NP2EO	1251.12	1227.37	1449.16	1425.42	2752.76	2729.01	7675.28	7653.76	2557.51	2557.51	140.78	119.26	34956.65	34948.47	4444.30	4420.55
NP3EO	3668.22	3636.28	1427.48	1395.54	1803.25	1771.32	5521.22	5510.71	1611.53	1577.46	110.63	100.12	13102.23	13081.25	5132.74	5100.80
NP4EO	2478.42	2426.45	853.50	801.54	1247.40	1195.43	2821.95	2813.34	968.01	918.89	112.49	103.88	3913.56	3889.00	2480.51	2428.54
NP5EO	614.70	549.88	731.56	666.74	246.63	181.81	3777.77	3777.77	369.31	304.09	96.29	96.29	2630.16	2597.55	1014.84	950.02
NP6EO	245.18	162.63	509.74	427.19	59.06	ND	4187.41	4187.41	124.68	39.99	178.51	178.51	1521.20	1478.85	261.18	178.64
NP7EO	163.58	55.63	374.53	266.57	ND	ND	2959.74	2959.74	99.67	ND	219.38	219.38	1156.66	1101.87	202.77	94.81
NP8EO	171.35	64.17	329.40	222.22	ND	ND	3294.24	3294.24	98.57	ND	243.97	243.97	1112.19	1057.45	186.76	79.58
NP9EO	137.61	27.77	269.08	159.23	ND	ND	3124.01	3124.01	107.05	ND	258.33	258.33	1094.67	1039.05	132.83	22.98
NP10EO	110.24	21.99	217.00	128.75	ND	ND	3124.56	3124.56	60.05	ND	235.65	235.65	1036.00	990.05	103.68	15.43
NP11EO	64.16	7.60	183.87	127.31	ND	ND	2601.25	2601.25	62.98	4.37	201.57	201.57	927.18	897.87	73.86	17.30
NP12EO	51.08	9.34	141.59	99.85	ND	ND	1924.16	1924.16	35.20	ND	161.72	161.72	830.76	808.01	52.99	11.25
NP13EO	27.07	27.07	114.40	114.40	ND	ND	1571.63	1571.63	36.48	36.48	108.59	108.59	690.76	690.76	36.41	36.41
NP14EO	ND	ND	83.10	83.10	ND	ND	1238.07	1238.07	ND	ND	73.00	73.00	583.69	583.69	14.54	14.54
NP15EO	ND	ND	57.80	57.80	ND	ND	880.44	880.44	ND	ND	55.62	55.62	451.63	451.63	0.00	ND
NP16EO	ND	ND	55.35	55.35	ND	ND	708.47	708.47	ND	ND	41.53	41.53	419.54	419.54	0.00	ND
NP17EO	ND	ND	45.50	45.50	ND	ND	443.98	443.98	ND	ND	26.59	26.59	356.92	356.92	0.00	ND
NP18EO	ND	ND	21.77	21.77	ND	ND	224.38	224.38	ND	ND	16.39	16.39	261.81	261.81	9.47	9.47
NP19EO	ND	ND	18.72	18.72	ND	ND	120.91	120.91	ND	ND	14.23	14.23	233.26	233.26	0.00	ND
Surrogate (% Recovery)																
¹³ C-NP1EO	ND		ND		ND		ND		ND		ND		ND		ND	
¹³ C-NP2EO	ND		1.0%		ND		3.9%		ND		0.4%		ND		ND	
¹³ C-NP3EO	17.6%		42.2%		30.4%		158.2%		24.0%		15.0%		46.9%		39.5%	
StdA*	31.2%		44.0%		25.8%		240.7%		26.2%		10.7%		73.9%		68.8%	

Notes: *Non-labeled surrogate polyoxyethylene-6-myristyl ether.

Table 18 Nonylphenol ethoxylate concentrations in receiving rivers of Alberta (ng/L). ND = Not Detected.

Target Analyte	North Saskatchewan River at Ft. Saskatchewan Bridge (downstream of effluents) 17/12/02		Bow River at Stiers Ranch (downstream of effluents) 15/01/03		Oldman River Southwest of Diamond City (downstream of effluent) 29/01/03		South Saskatchewan River Upstream of Medicine Hat (upstream of effluent) 23/01/03		Red Deer River at Red Deer (downstream of effluent) 22/01/03	
	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected	Concentration (ng/L)	Blank Corrected
NP1EO	75.12	75.12	66.45	66.45	ND	ND	193.72	193.72	126.35	126.35
NP2EO	109.77	86.02	141.05	119.52	249.91	226.16	240.29	232.12	129.99	106.24
NP3EO	95.12	63.18	82.18	71.68	192.57	160.64	189.64	168.66	132.12	100.18
NP4EO	82.72	30.76	63.57	54.96	349.24	297.27	105.95	81.39	104.51	52.55
NP5EO	49.60	ND	58.11	58.11	367.19	302.37	69.87	37.26	70.52	5.70
NP6EO	23.81	ND	89.75	89.75	483.84	401.30	48.66	6.31	63.47	ND
NP7EO	20.09	ND	123.77	123.77	641.02	533.06	50.69	ND	73.98	ND
NP8EO	22.68	ND	132.59	132.59	628.99	521.81	46.52	ND	71.14	ND
NP9EO	18.87	ND	132.34	132.34	647.47	537.62	44.08	ND	66.46	ND
NP10EO	16.15	ND	114.64	114.64	467.61	379.35	42.08	ND	56.14	ND
NP11EO	10.38	ND	98.11	98.11	381.06	324.50	33.57	4.26	50.98	ND
NP12EO	7.38	ND	73.29	73.29	348.18	306.43	22.40	ND	35.04	ND
NP13EO	ND	ND	51.15	51.15	ND	ND	13.27	13.27	24.21	24.21
NP14EO	ND	ND	34.95	34.95	ND	ND	9.59	9.59	20.42	20.42
NP15EO	ND	ND	24.50	24.50	ND	ND	5.83	5.83	11.69	11.69
NP16EO	ND	ND	19.77	19.77	ND	ND	4.77	4.77	10.15	10.15
NP17EO	ND	ND	10.54	10.54	ND	ND	ND	ND	8.64	8.64
NP18EO	ND	ND	9.26	9.26	ND	ND	4.91	4.91	8.65	8.65
NP19EO	ND	ND	7.94	7.94	ND	ND	ND	ND	9.87	9.87
Nonylphenol Equivalents [†] (Including Nonylphenol ^{**})	-	127.54	-	653.56	-	1404.66	-	479.16	-	232.17
Surrogate (% Recovery)										
¹³ C-NP1EO	ND		ND		ND		ND		ND	
¹³ C-NP2EO	1.5%		0.4%		ND		1.2%		0.7%	
¹³ C-NP3EO	51.6%		19.5%		1.8%		35.5%		25.9%	
StdA*	46.1%		54.7%		1.3%		34.9%		28.3%	

Notes: *Non-labeled surrogate polyoxyethylene-6-myristyl ether.

[†]Sum of toxic equivalents for NP1EO through NP19EO.

^{**}From Table 13.

8.0 FIGURES

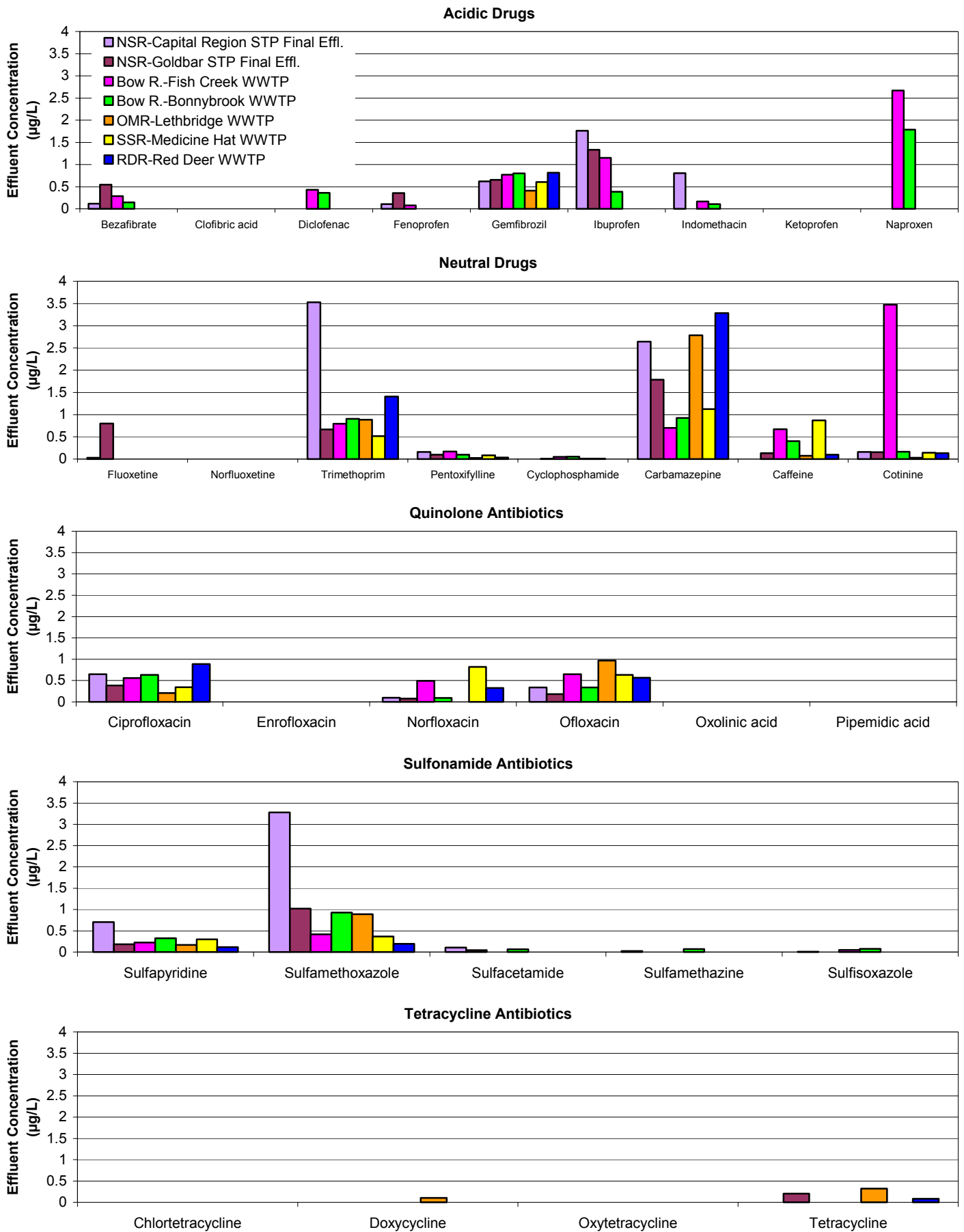


Figure 1 Pharmaceutical concentrations in WWTP effluents of Alberta.

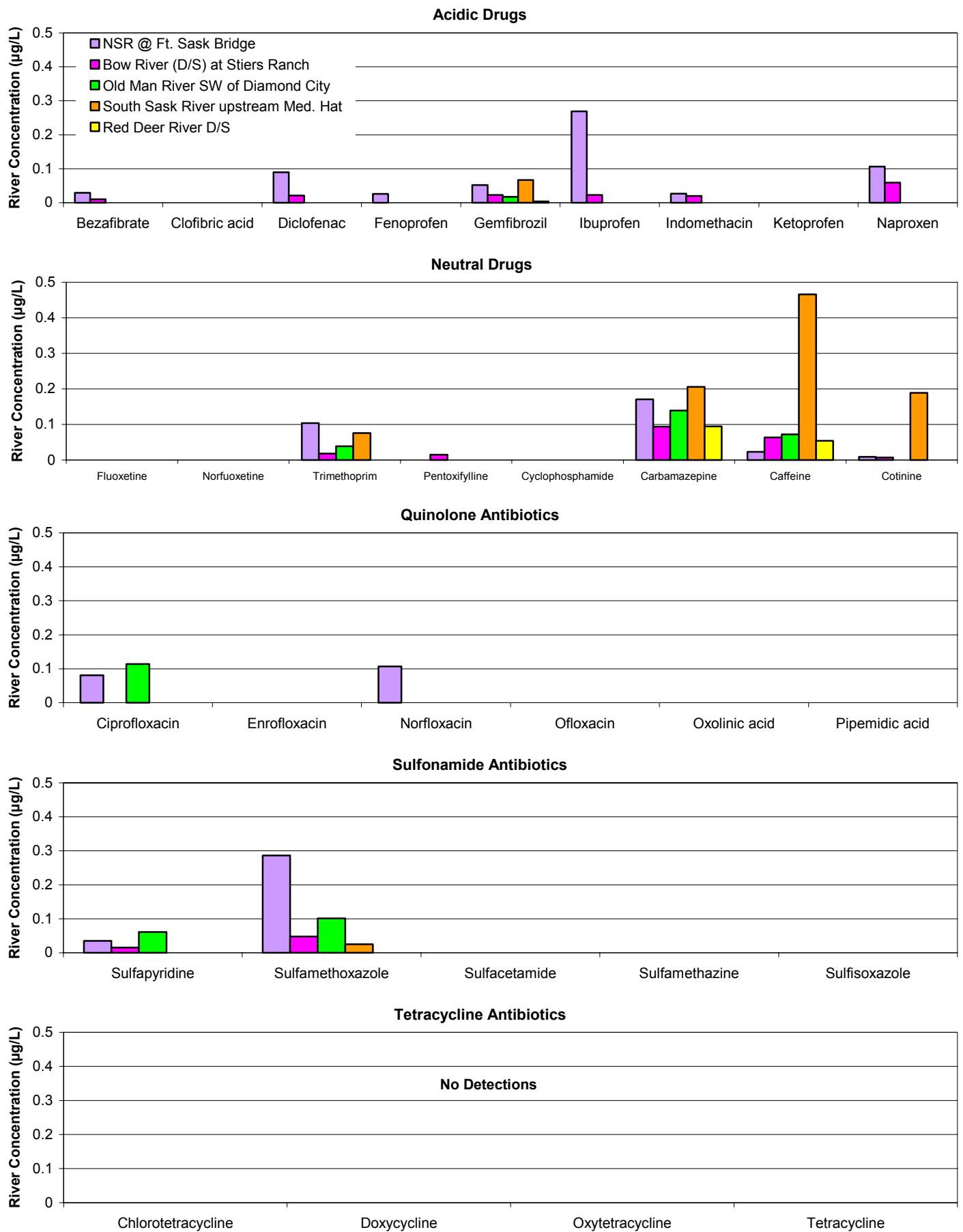


Figure 2 Pharmaceutical concentrations in receiving rivers of Alberta.

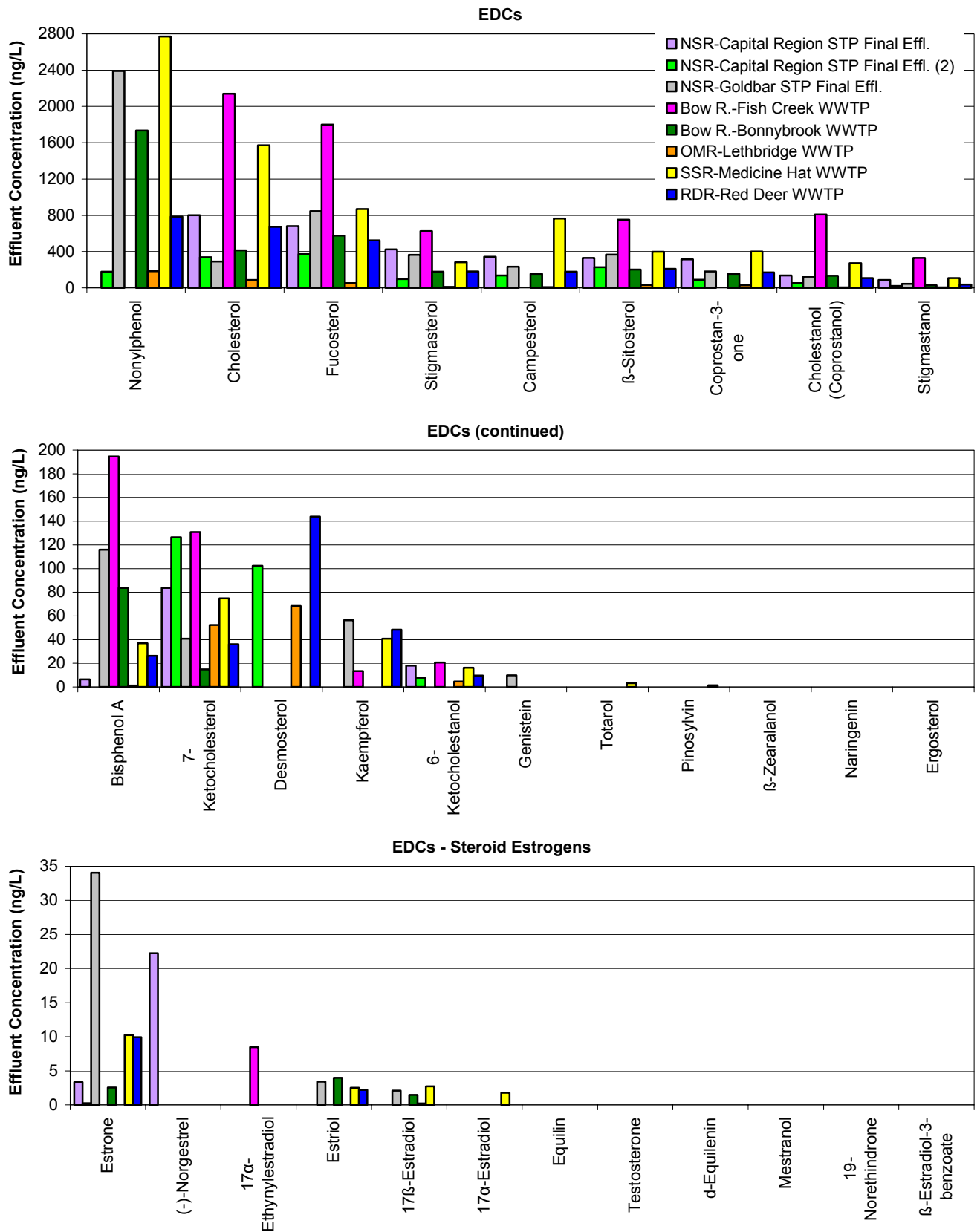


Figure 3 EDC concentrations in WWTP effluents of Alberta (recovery corrected data).

Note scale differences on y-axes.

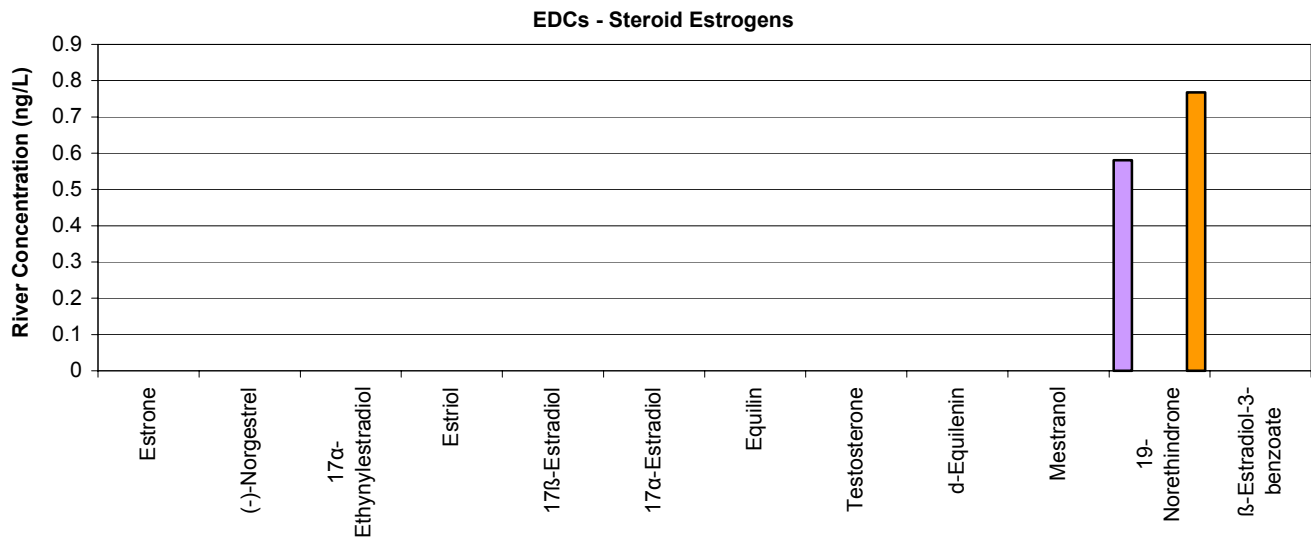
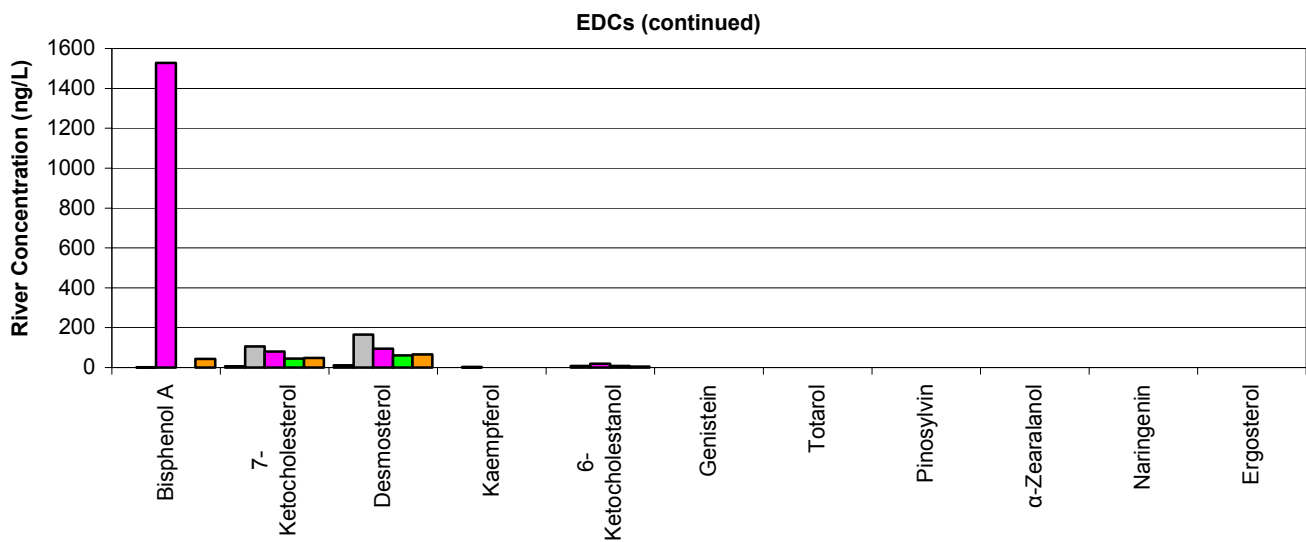
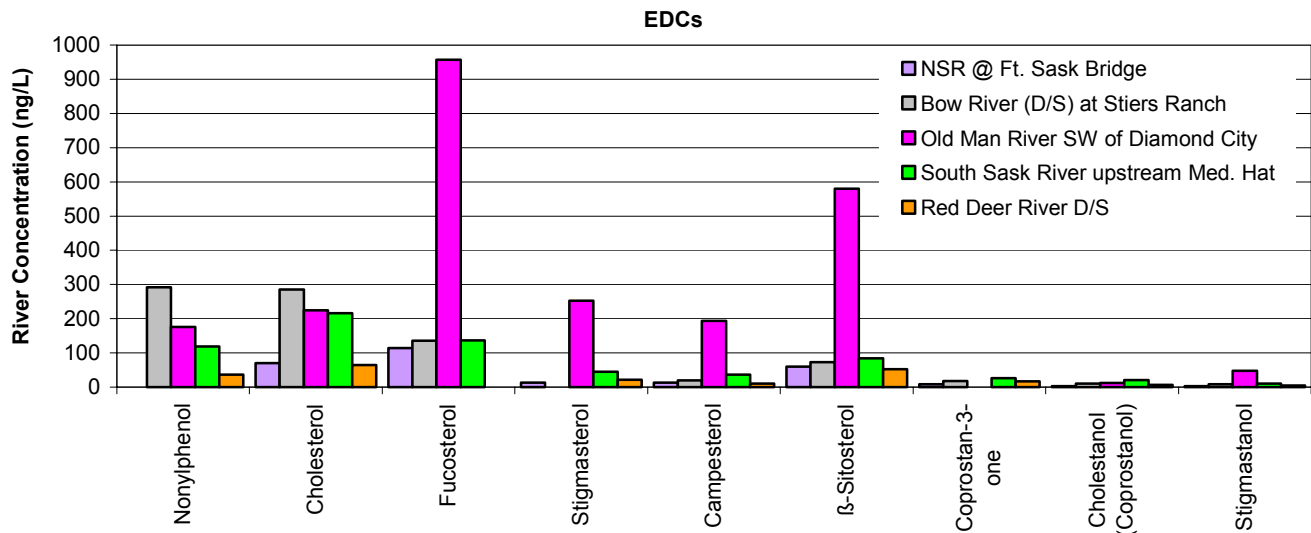


Figure 4 EDC concentrations in receiving rivers of Alberta (recovery corrected data).

Note scale differences on y-axes.

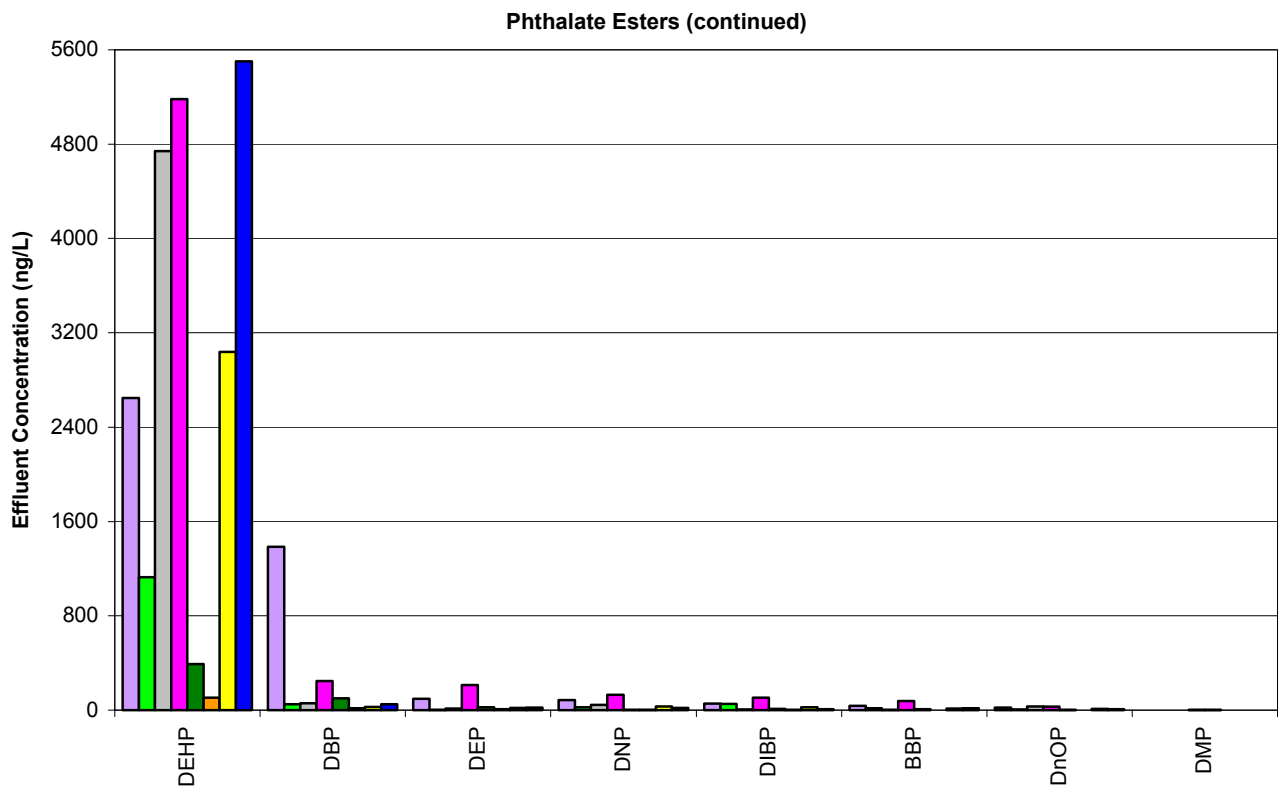
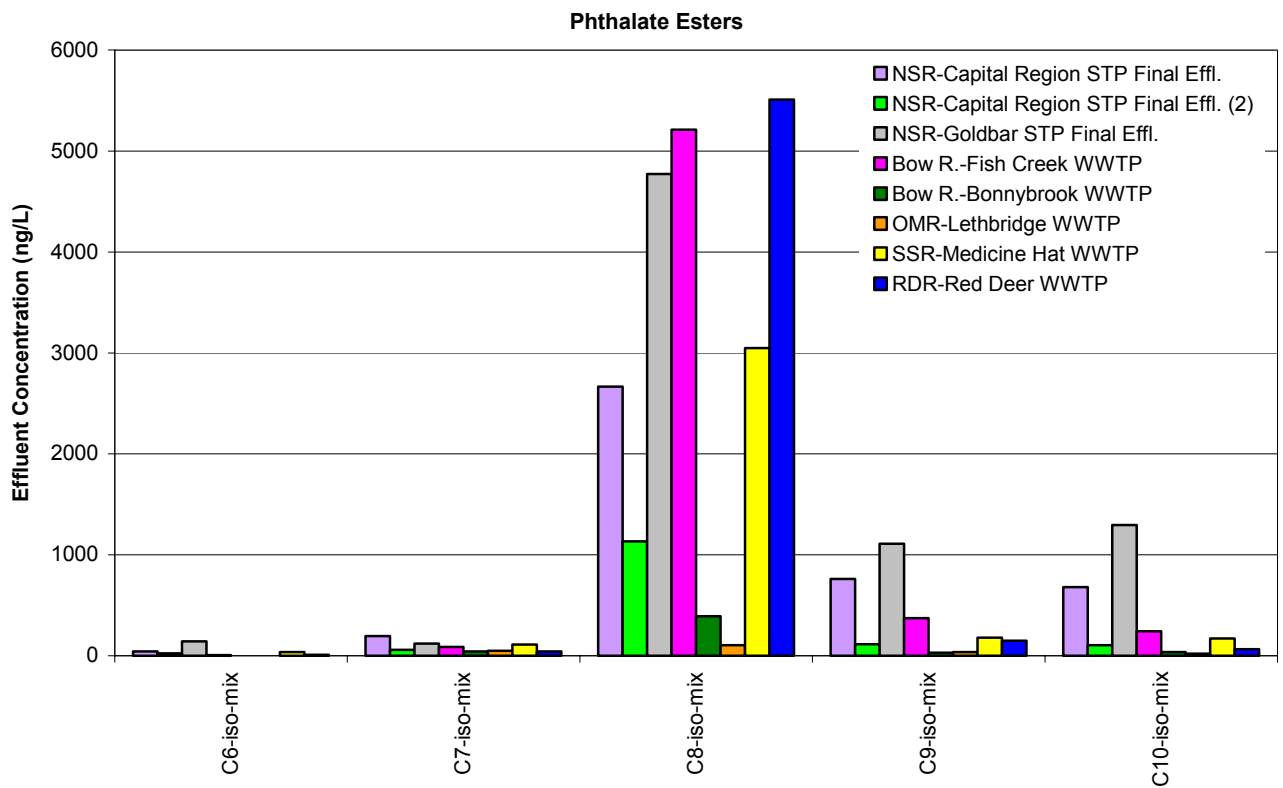


Figure 5 Phthalate ester concentrations in WWTP effluents of Alberta (recovery corrected data). Note scale differences on y-axes.

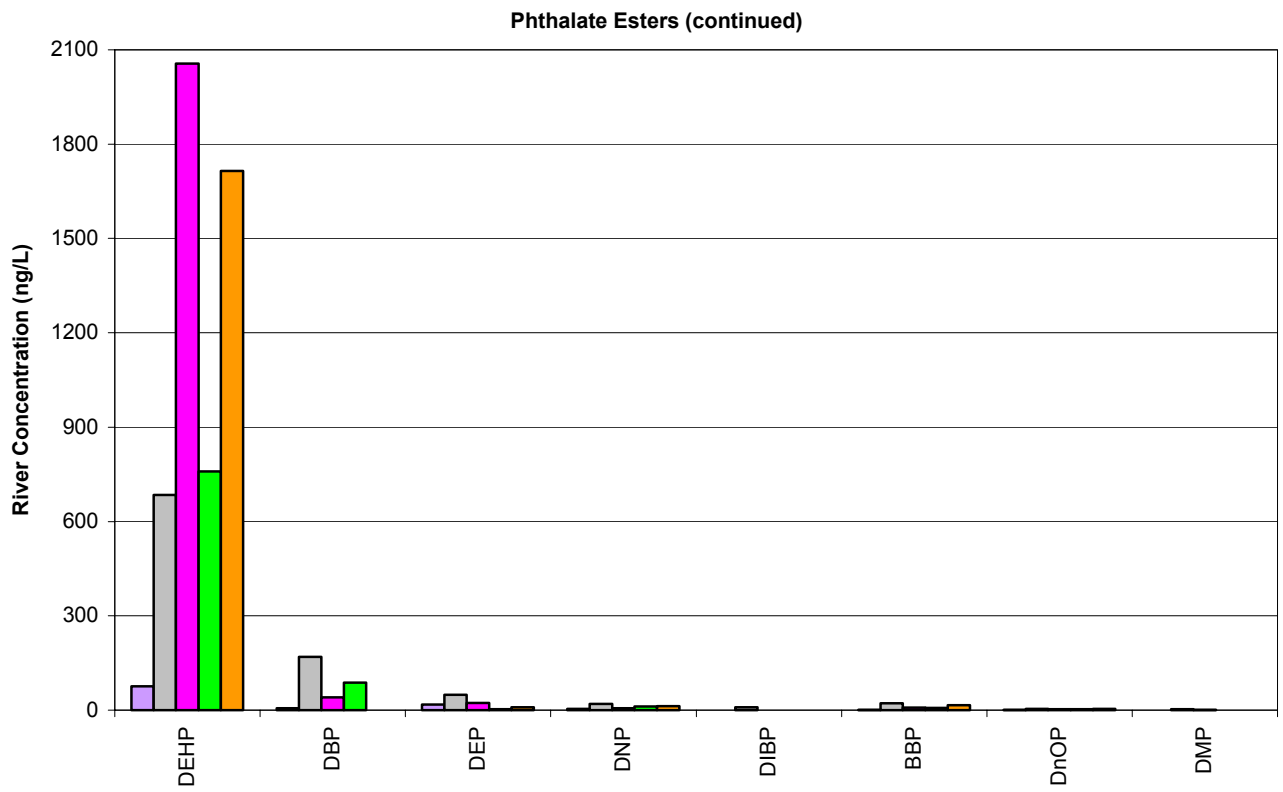
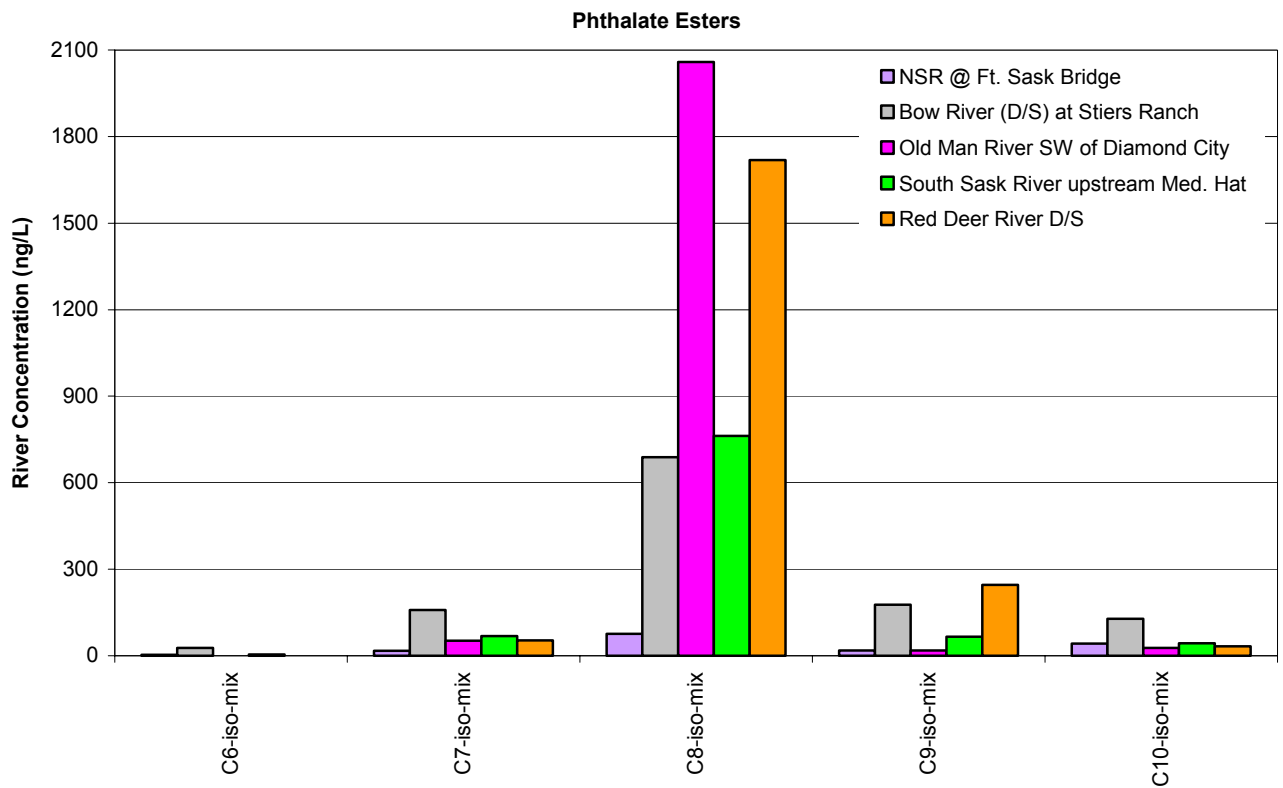


Figure 6 Phthalate ester concentrations in receiving rivers of Alberta (recovery corrected data).

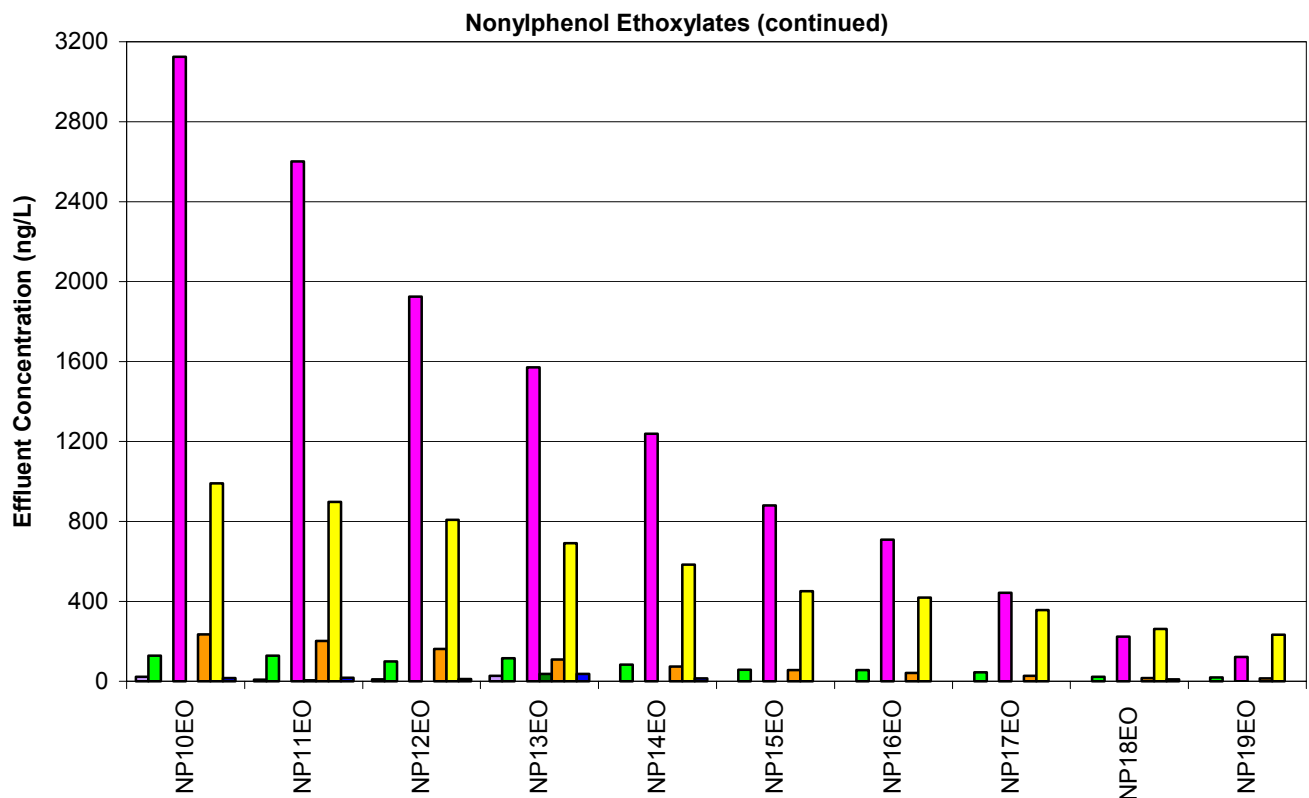
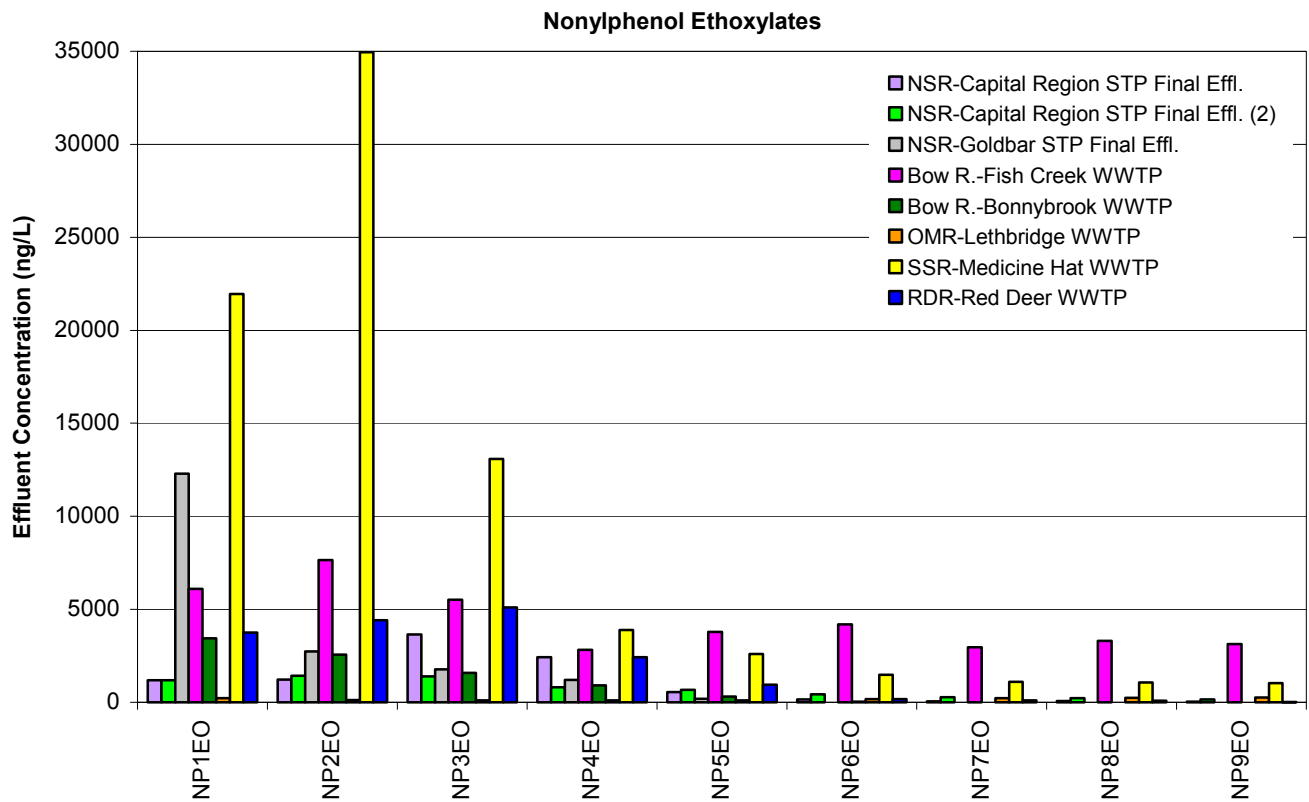


Figure 7 Nonylphenol ethoxylate concentrations in WWTP effluents of Alberta (recovery corrected data). Note scale differences on y-axes.

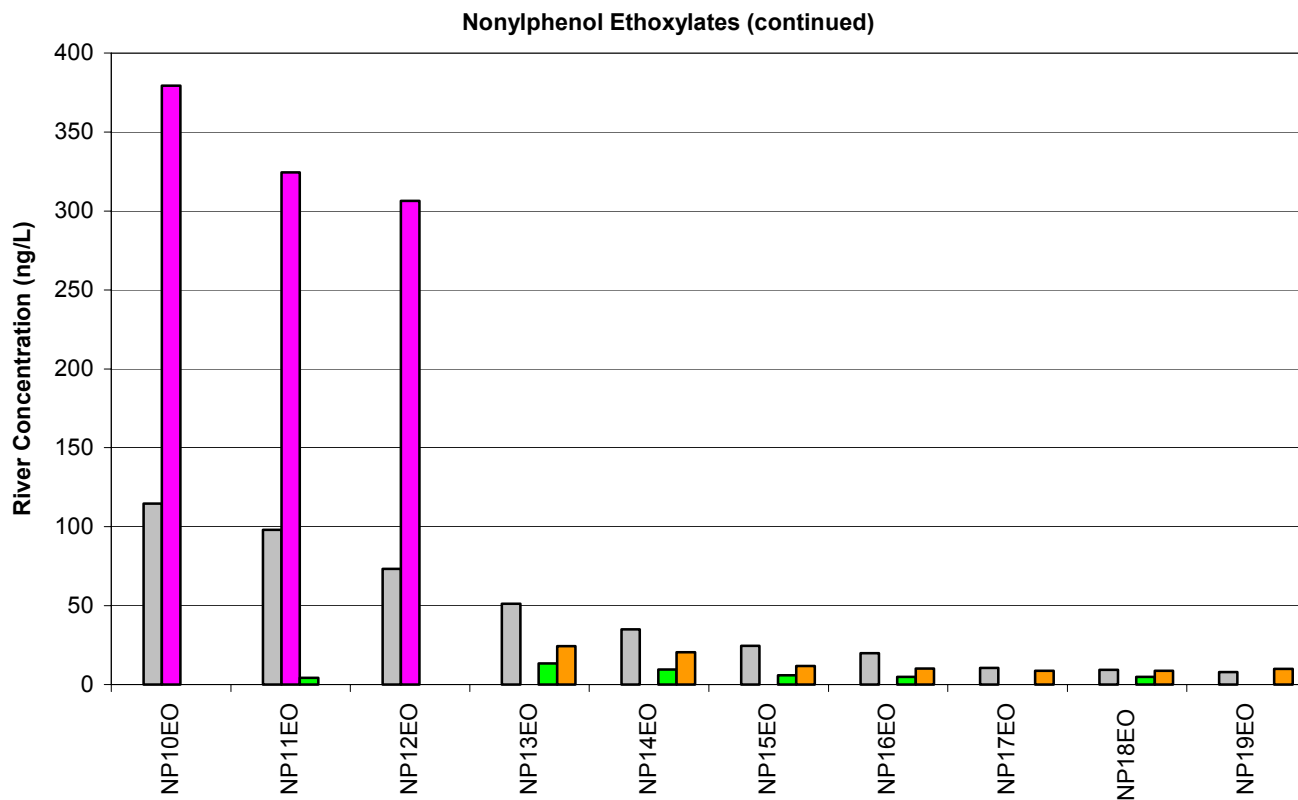
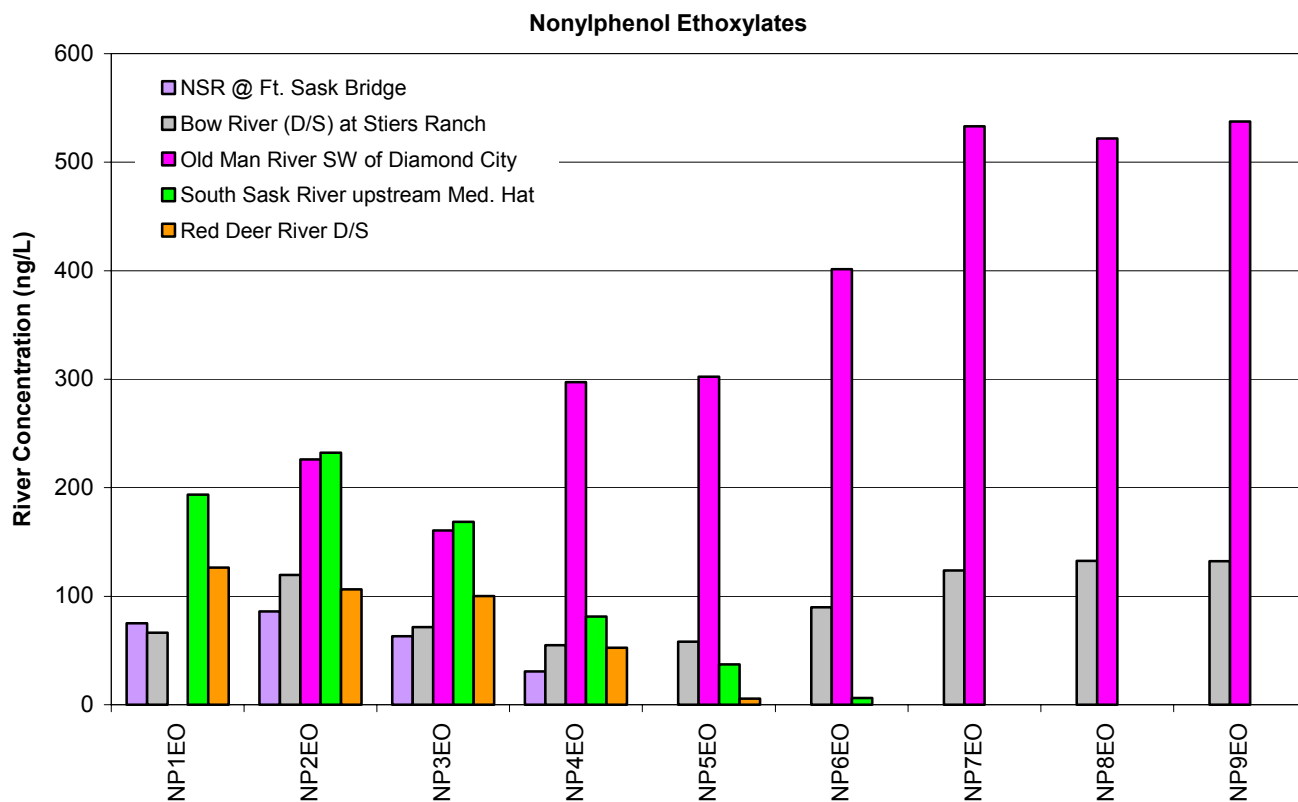


Figure 8 Nonylphenol ethoxylate concentrations in receiving rivers of Alberta (recovery corrected data). Note scale difference on y-axes.

9.0 APPENDICES

Appendix I Median recoveries of spiked surrogates from samples of WWTP effluent and receiving river water collected in Alberta.

Wastewater Treatment Plant Effluents							
EDCs		Phthalate Esters		Phthalate Monoesters		Nonylphenol Ethoxylates	
Surrogate	Median % Recovery	Surrogate	Median % Recovery	Surrogate	Median % Recovery	Surrogate	Median % Recovery
¹³ C-Nonylphenol	0.37	d-4 DMP	43.70	NA	NA	¹³ C-NP1EO	ND
DnOP-d4	61.25	d-4 DBP	68.20	NA	NA	¹³ C-NP2EO	ND
		d-4 DOP	84.10	NA	NA	¹³ C-NP3EO	34.95
						StdA	37.60
Receiving Rivers							
EDCs		Phthalate Esters		Phthalate Monoesters		Nonylphenol Ethoxylates	
Surrogate	Median % Recovery	Surrogate	Median % Recovery	Surrogate	Median % Recovery	Surrogate	Median % Recovery
¹³ C-Nonylphenol	0.35	d-4 DMP	31.50	NA	NA	¹³ C-NP1EO	ND
DnOP-d4	74.60	d-4 DBP	75.60	NA	NA	¹³ C-NP2EO	0.70
		d-4 DOP	74.40	NA	NA	¹³ C-NP3EO	25.90
						StdA	34.90

Notes: NA = Samples were not spiked.
 ND = Compound not detected.
 StdA = polyoxyethylene-6-myristyl ether

Appendix II EDC concentrations in blank (type 1, laboratory grade) water samples.

Target Analyte	IOS Procedural Blank		IOS Procedural Blank 1		IOS Procedural Blank 2		IOS Procedural Blank 3		ETL Procedural Blank	
	Concentration (ng/L)	Sample Detection Limit (ng/L)	Concentration (ng/L)	Sample Detection Limit (ng/L)	Concentration (ng/L)	Sample Detection Limit (ng/L)	Concentration (ng/L)	Sample Detection Limit (ng/L)	Concentration (ng/L)	Sample Detection Limit (ng/L)
Nonylphenol	ND	0.351	41.392	1.843	54.356	0.653	21.537	12.340	6.414	3.200
Bisphenol A	2.192	0.017	4.964	0.034	41.771	0.096	0.662	0.019	0.571	0.023
Totanol	ND	0.006	ND	0.005	ND	0.003	ND	0.016	ND	0.012
Pinosylvin	ND	0.008	ND	0.005	ND	0.024	ND	0.011	ND	0.015
Estrone	0.040	0.011	ND	0.006	ND	0.008	ND	0.016	ND	0.021
Equilin	ND	0.012	ND	0.020	ND	0.021	ND	0.142	ND	0.143
17 α -Estradiol	ND	0.096	ND	0.005	ND	0.004	ND	0.259	ND	0.191
Testosterone	ND	0.214	ND	0.141	ND	0.092	ND	0.356	ND	0.570
17 β -Estradiol	ND	0.003	ND	0.009	ND	0.005	ND	0.008	ND	0.015
d-Equilenin	ND	0.045	ND	0.007	ND	0.011	ND	0.053	ND	0.010
Mestranol	ND	0.030	ND	0.023	ND	0.016	ND	0.036	ND	0.065
19-Norethindrone	ND	0.082	ND	0.120	ND	0.071	ND	0.300	ND	0.278
17 α -Ethinylestradiol	ND	0.022	ND	0.022	ND	0.038	ND	0.094	ND	0.054
(-)-Norgestrel	ND	0.128	ND	0.418	ND	0.334	ND	0.708	ND	0.695
α -Zearalanol	ND	1.008	ND	4.359	ND	1.011	ND	4.752	ND	8.167
Naringenin	ND	0.158	ND	0.270	ND	0.128	ND	0.293	ND	0.217
Estriol	0.017	0.011	ND	0.037	ND	0.042	ND	0.108	ND	0.090
Genistein	ND	0.123	ND	0.103	ND	0.362	ND	0.353	ND	0.469
Kaempferol	ND	0.015	ND	0.795	ND	0.549	ND	2.165	ND	1.345
Coprostan-3-one	ND	0.460	ND	0.444	0.595	0.409	ND	2.345	ND	1.756
Cholesterol	1.726	0.132	ND	0.071	ND	0.117	0.657	0.136	3.698	0.211
Cholestanol*	ND	0.039	ND	0.115	ND	0.101	ND	0.162	ND	0.226
Desmosterol	ND	0.526	ND	0.515	ND	0.394	ND	1.483	ND	2.700
Ergosterol	ND	0.805	ND	0.608	ND	0.827	ND	2.888	ND	3.042
Campesterol	ND	0.216	ND	0.097	ND	0.028	ND	0.634	ND	0.558
Stigmasterol	ND	0.133	ND	0.056	ND	0.215	ND	0.638	ND	0.450
β -Sitosterol	ND	0.202	0.548	0.537	ND	0.463	ND	0.448	ND	0.507
Fucosterol	ND	1.584	ND	2.699	ND	5.584	ND	2.862	ND	3.348
Stigmastanol	ND	0.088	ND	0.201	ND	0.036	ND	0.789	ND	0.471
6-Ketocholestanol	ND	0.033	ND	0.081	ND	0.031	ND	0.320	ND	0.185
7-Ketocholesterol	ND	0.062	ND	0.219	ND	0.146	ND	0.428	ND	0.441
β -Estradiol-3-benzoate	ND	0.032	ND	0.232	ND	0.100	ND	0.653	ND	0.349
Samples for which blank corrections were applied:	Fish Creek WWTP		Alberta Environment		Alberta Environment Bonnybrook WWTP City of Medicine Hat		Alberta Environment Bonnybrook WWTP City of Medicine Hat		Alberta Environment Bonnybrook WWTP Fish Creek WWTP City of Medicine Hat	

Notes: City of Medicine Hat = Medicine Hat WWTP & South Saskatchewan River upstream of Medicine Hat.

Alberta Environment = All other samples, excluding Fish Creek WWTP, Bonnybrook WWTP, & Medicine Hat.

ND = Compound not detected.

IOS = Institute of Ocean Sciences

ETL = Envirotest Laboratories Ltd.

*Also known as coprostanol.

Appendix III Phthalate ester concentrations in blank (type 1, laboratory grade) water samples.

Target Analyte	Batch 184				Batch 191					
	IOS Procedural Blank 1		IOS Procedural Blank 2		IOS Procedural Blank 1		IOS Procedural Blank 2		ETL Procedural Blank	
	Concentration (ng/L)	Sample Detection Limit (ng/L)	Concentration (ng/L)	Sample Detection Limit (ng/L)	Concentration (ng/L)	Sample Detection Limit (ng/L)	Concentration (ng/L)	Sample Detection Limit (ng/L)	Concentration (ng/L)	Sample Detection Limit (ng/L)
C6-iso-mix	ND	1.9	ND	1.8	ND	2.8	ND	3.0	ND	3.3
C7-iso-mix	ND	2.4	ND	2.1	ND	3.5	ND	3.8	ND	3.6
C8-iso-mix	4.8	0.4	4.6	0.4	26.4	0.3	15.9	0.4	11.1	3.3
C9-iso-mix	ND	3.4	ND	3.2	ND	3.4	ND	3.6	ND	2.9
C10-iso-mix	ND	4.6	ND	5.0	ND	4.0	ND	4.8	ND	4.0
DMP	1.0	0.04	0.7	0.03	0.2	0.1	0.1	0.04	0.3	0.1
DEP	12.1	0.1	9.1	0.1	3.9	0.1	2.7	0.1	1.8	0.1
DIBP	6.3	0.1	5.7	0.0	5.7	0.1	4.0	0.1	6.9	0.1
DBP	38.9	0.04	33.4	0.1	79.4	0.2	53.2	0.1	24.0	0.2
BBP	2.2	0.1	2.1	0.1	13.7	0.1	7.8	0.1	2.9	0.4
DEHP	4.8	0.2	4.3	0.2	25.9	0.2	14.2	0.2	10.8	3.2
DnOP	ND	0.2	0.3	0.2	0.5	0.1	1.7	0.2	0.3	0.1
DNP	ND	0.2	ND	0.2	ND	0.2	1.5	0.2	ND	0.2
Surrogate (% Recovery)										
d-4 DMP	88.3%		89.0%		82.6%		86.1%		NA	
d-4 DBP	102.0%		99.4%		93.0%		94.7%		NA	
d-4 DOP	90.3%		82.2%		78.4%		78.3%		NA	

Notes: IOS = Institute of Ocean Sciences
 ETL = Envirotest Laboratories Ltd.
 ND = Compound not detected.
 NA = Sample was not spiked.

Appendix IV Phthalate monoester concentrations in blank (type 1, laboratory grade) water samples.

Target Analyte	IOS Instrument Blank		Solvent/Glassware/ ETL Laboratory Blank	
	Concentration (ng/L)	Sample Detection Limit (ng/L)	Concentration (ng/L)	Sample Detection Limit (ng/L)
MMP	ND	5.0	ND	5.0
MEP	ND	5.0	ND	5.0
MButP	ND	6.0	ND	6.0
M C6-iso-mix	ND	12.0	ND	12.0
MBzP	ND	6.0	ND	6.0
M C7-iso-mix	ND	7.0	ND	7.0
M C8-iso mix (MEHP+MnOP)	ND	4.2	ND	4.2
M C9-iso-mix	ND	6.3	ND	6.3
M C10-iso-mix	ND	7.3	ND	7.3

Notes: ND = Compound not detected.
 IOS = Institute of Ocean Sciences
 ETL = Envirotest Laboratories Ltd.

Appendix V Nonylphenol ethoxylate concentrations in blank (type 1, laboratory grade) water samples.

Target Analyte	IOS Procedural Blank		IOS Procedural Blank1		IOS Procedural Blank2		IOS Procedural Blank3		ETL Procedural Blank	
	Concentration (ng/L)	Sample Detection Limit (ng/L)	Concentration (ng/L)	Sample Detection Limit (ng/L)	Concentration (ng/L)	Sample Detection Limit (ng/L)	Concentration (ng/L)	Sample Detection Limit (ng/L)	Concentration (ng/L)	Sample Detection Limit (ng/L)
NP1EO	ND	26.705	ND	20.306	ND	29.150	ND	26.705	ND	22.088
NP2EO	16.353	9.072	47.493	26.418	ND	79.094	16.353	9.072	21.523	12.671
NP3EO	7.891	3.972	29.807	13.447	34.071	15.641	7.891	3.972	10.509	4.212
NP4EO	ND	7.466	54.814	16.779	49.115	21.494	ND	7.466	8.612	6.920
NP5EO	ND	6.945	64.423	13.468	65.223	14.387	ND	6.945	ND	7.341
NP6EO	ND	9.937	80.398	42.874	84.695	19.379	ND	9.937	ND	12.486
NP7EO	ND	10.126	106.335	56.741	109.578	25.732	ND	10.126	ND	12.239
NP8EO	ND	11.195	104.882	28.592	109.477	32.490	ND	11.195	ND	15.154
NP9EO	ND	8.474	108.462	22.080	111.236	20.313	ND	8.474	ND	8.958
NP10EO	ND	6.901	84.606	20.396	91.904	29.751	ND	6.901	ND	7.482
NP11EO	ND	6.194	54.504	17.884	58.616	38.982	ND	6.194	ND	6.980
NP12EO	ND	4.581	37.987	32.494	45.497	24.512	ND	4.581	ND	4.374
NP13EO	ND	4.767	ND	19.227	ND	15.975	ND	4.767	ND	7.576
NP14EO	ND	6.683	ND	5.784	ND	18.590	ND	6.683	ND	7.770
NP15EO	ND	6.222	ND	8.156	ND	6.949	ND	6.222	ND	6.597
NP16EO	ND	5.336	ND	10.887	ND	7.992	ND	5.336	ND	5.707
NP17EO	ND	5.704	ND	7.726	ND	11.408	ND	5.704	ND	6.489
NP18EO	ND	3.910	ND	7.881	ND	7.784	ND	3.910	ND	3.872
NP19EO	ND	4.224	ND	10.586	ND	4.746	ND	4.224	ND	3.180
Samples for which blank corrections were applied:	Fish Creek WWTP		Alberta Environment		Alberta Environment Bonnybrook WWTP City of Medicine Hat		Alberta Environment Bonnybrook WWTP City of Medicine Hat		Alberta Environment Bonnybrook WWTP Fish Creek WWTP City of Medicine Hat	

***Notes:** City of Medicine Hat = Medicine Hat WWTP & South Saskatchewan River upstream of Medicine Hat.
 Alberta Environment = All other samples, excluding Fish Creek WWTP, Bonnybrook WWTP, & Medicine Hat.
 ND = Compound not detected.
 IOS = Institute of Ocean Sciences
 ETL = Envirotest Laboratories Ltd.