Results of caffeine testing in water from select Pigeon Lake inflows

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1.0 Executive Summary

Samples from four Pigeon Lake inflows were collected on August 12, 2003 by *Aqua*lity Environmental Consulting Ltd. for caffeine and other organic compound analyses. The four sampled sites were inflows of Norris Beach, Sunset Harbour, Grandview Heights, and Poplar Beach. The purpose of this work was to determine: (i) if untreated human sewage is entering the lake by using caffeine as an indicator for human sewage and (ii) if there are other organic compounds of concern that may suggest impacts from industrial or other activities.

Caffeine is an ideal indicator for detecting human waste in the natural environment. Because caffeine has no natural environmental source, and no other animals ingest caffeine, we can assume that any caffeine found in surface waters originates from human sewage. Humans consume caffeine from a variety of sources including caffeinated beverages (coffee, tea, soft drinks) foods (chocolate, pastries, dairy desserts), analgesics (cough, cold and headache medicines) and pharmaceuticals (used as a stimulant in cardiac, cerebral and respiratory drugs and as a diuretic). Caffeine is found at predictable concentration in the human wastes of many countries, including Canada, which allows us to calculate approximate dilutions and loadings (Buerge et al. 2003). The detection limits of this study were 0.5 ppb (0.5 ug/L).

Caffeine was not detected at any of the four inflow locations sampled on Pigeon Lake. The results could mean one of three things: (i) there is currently no raw human sewage being deposited in the tested inflows, (ii) sample collection may have occurred too long after a sewage release; or (iii) detection limits were not sensitive enough to detect diluted caffeine levels. Even though the 0.5 ug/L detection limit can measure dilutions up to 82-fold, possible sewage inputs into Pigeon Lake may be diluted to a greater degree than could be detected by the current analytical technique. Further refinement of the analytical technique to improve detection limits to the nanogram/L range (ng/L) is recommended for future samplings.

2.0 Introduction

Pigeon Lake is a popular recreational lake 60 km southwest of Edmonton, Alberta (53^{o} 01´ N 114^{o} 02´ W). The lake has a surface area of 96.7 km^{2}, an upland watershed area of 187 km^{2}, a maximum depth of 9.1 m and a mean depth of 6.2 m (Michell and Prepas, 1990).

There are over 3000 private recreational lots around the lake, with an estimated summer population of 9563 (West Central Planning Agency, 2003). Two Provincial Parks, Ma-Me-O Beach and Pigeon Lake Provincial Park, and a number of other campgrounds, boat launches, and picnic areas also exist on the shores of the lake. The lake supports a number of recreational activities, including swimming, sailing, sport fishing and commercial fishing.

Pigeons Lake's watershed area is approximately twice the size of the lake's surface area, which is a small ratio. Typically, lakes have a watershed area ten times or more larger than their surface area. Approximately half of the land base in the watershed is cleared for agriculture, and supports feed grains and hay crops. There are also a number of cow-calf operations in the drainage basin and two oil fields, the Pembina and Bonnie Glen Fields.

Due to speculation of sewage dumping into some of the tributaries of Pigeon Lake and land application of sewage wastes onto agricultural fields, *Aqua*lity Environmental Consulting Ltd. (*Aqua*lity) was contracted by a private resident at Pigeon Lake to collect water samples for caffeine analysis. Caffeine is an ideal indicator for detecting human waste for several reasons. Because caffeine has no natural source in the environment, and no other animals ingest caffeine, we can assume that any concentrations of caffeine found in surface waters must originate from human sewage. Humans consume caffeine from a variety of sources including caffeinated beverages (coffee, tea, soft drinks) foods (chocolate, pastries, dairy desserts), analgesics (cough, cold and headache medicines) and pharmaceuticals (used as a stimulant in cardiac, cerebral and respiratory drugs and as a diuretic).

Further, caffeine is found in North American sewage wastes at predictable concentrations, which allows us to calculate approximate dilutions and loadings. While routine caffeine analysis is not done in Canada, Alberta Research Council (ARC) in Vegreville was contacted to establish an analytical procedure for use by *Aqua*lity, and provided detection limits for caffeine to 0.5 ppb (0.5 µg/L).

Because caffeine levels are documented in North American urinary wastes, we can back-calculate dilution rates and loadings of sewage in natural waters. Urinary caffeine levels in caffeinated soda drinkers (an average of 2 servings per day) are 1500 µg/L. Based on a normal urine volume of 1400 mL/day, a frequency of 5 urinations per day and a flush volume of 9.8 L, raw urinary sewage should contain 41 µg/L of caffeine. Therefore, our analytical technique is

able to detect raw sewage diluted in freshwater up to 82 times. A benefit of the ARC technique for analyzing caffeine is that a suite of other organic compounds such as phthalate esters can be detected along with caffeine (see Appendix A).

3.0 Methods

3.1 Field Collections

Pigeon Lake was sampled by *Aqua*lity on August 13, 2003 following a long period without precipitation. Sites were chosen to match the five sites currently being monitored by AENV for other routine water quality analyses. Of the five sites monitored by AENV, Mitchell Beach Creek had no flowing water and could not be sampled during our August visit. The remaining four inflow sites contained water and were sampled: Poplar Beach, Norris Beach, Sunset Harbour, and Grandview Heights (Figure 1).

Only inflow sites were selected for sampling. This decision was based on the expectation that inflows would be the most probable source of sewage entering the lake, and therefore the best location to search for detectable concentrations. Ultra-clean glass 1L amber collection bottles were provided by ARC Vegreville for sample collection. Samples were collected by holding bottles upstream (into the current) in the middle of the water column until full. Collections were made to avoid stirred up sediments, algae and other debris from entering the collection bottles. Bottles were shipped overnight in coolers with icepacks, for next morning delivery to ARC.

3.2 Laboratory Analysis

The Alberta Research Council (ARC) in Vegreville, Alberta was contacted in May, 2003 to provide caffeine analyses for *Aqua*lity. As ARC previously did not calibrate on this compound, a laboratory grade standard was requested and purchased by *Aqua*lity for calibration. Using gas chromatrograph—mass spectrometry (GC—MS) under total ion chromatogram (TIC) conditions, ARC was able to detect caffeine to 0.5 ppb (ug/L). This technique also identifies other hydrocarbon species, such as phthalate esters during the analysis.

4.0 Results

4.1 Results Summary

None of the four samples analyzed contained detectable levels of caffeine at the limit of 0.5 ppb. However, several phthalate esters (Bis (2-ethylhexyl) phthalate, butylbenzylphthalate, and Di-n-

butylphthalate) and polycyclic aromatic hydrocarbons (PAHs) (acenapthene, flouranthene, phenanthrene and pyrene) were detected in the samples (Table 1). Of these compounds, only pyrene concentrations at Poplar Beach exceeded the CCME water quality guideline for the protection of aquatic life.

The raw laboratory results from ARC appear in Appendix A.

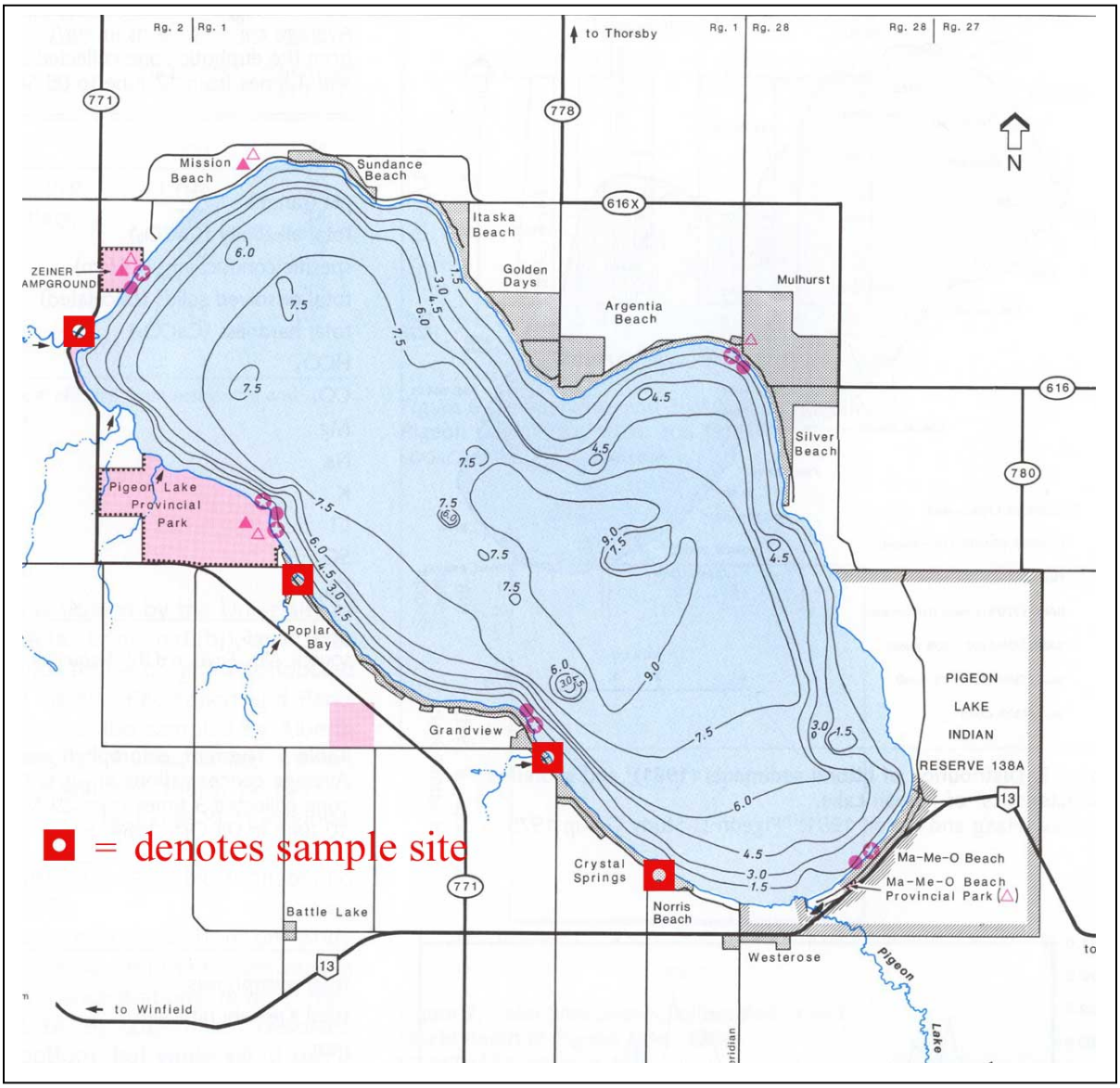

Figure 1: Inflow sites sampled on August 13, 2003 at Pigeon Lake. Samples were analyzed for caffeine to determine if human sewage is entering Pigeon Lake at these locations.

Table 1: Organic contaminants (phthalate esters and polycyclic aromatic hydrocarbons) detected in water samples collected from inflows of Pigeon Lake, Alberta in August of 2003.

Compound	CCME Guidelines[1] (ug/L)	Poplar Beach (ug/L)	Norris Beach (ug/L)	Sunset Harbour (ug/L)	Grandview Heights (ug/L)
Acenaphthene	5.8	0.0	0.1	0.0	0.0
Bis (2-ethylhexyl) phthalate	----	5.6	1.8	2.2	0.8
Butylbenzylphthalate	----	0.0	0.0	0.1	0.0
Di-n-butylphthalate	19	0.5	0.6	0.8	1.1
Flouranthene	3.0	0.1	0.0	0.0	0.0
Phenanthrene	0.4	0.2	0.1	0.0	0.0
Pyrene	0.025	**0.1**	0.0	0.0	0.0

[1]Canadian Council of Ministers of the Environment, Guidelines for the Protection of Freshwater Life (2003).

5.0 Conclusions and Recommendations

5.1 Summary of Caffeine Study

None of the four sites selected for this study were found to contain detectable levels of caffeine. These results could mean one of three things: (i) there is currently no raw human sewage being deposited in the tested inflows, (ii) sample collection may have occurred too long after a sewage release; or (iii) detection limits were not sensitive enough to detect diluted caffeine levels.

Because of the lack of precipitation prior to our samplings, we assume that inflows were experiencing baseflow (i.e. contribution of water from groundwater only) conditions, and did not contain any surface water from upland catchment runoff. If caffeine were to be detected in the inflows streams, it would suggest groundwater contamination by human sewage wastes.

Even though the 0.5 ug/L detection limit can measure dilutions up to 82-fold, potential sewage inputs into Pigeon Lake may be diluted to a greater degree than could be detected with the current analytical technique. Further refinement of the analytical technique to improve detection limits to the nanogram per liter range (ng/L) is recommended for future studies.

5.2 Fate of Caffeine in the Environment

Modern sewage treatment facilities are highly effective at removing caffeine with 80-100% removal in modern systems (Buerge et al. 2003). Caffeine is removed from lake systems through lake flushing and physical, chemical and biological degradation. Of all these processes,

photodegradation by direct and indirect photolysis removes caffeine most effectively (Buerge et al. 2003). When wastewater is released into a sunny environment, caffeine has a half life of approximately 12 days (Buerge et al. 2003).

5.2 Summary of Organic Pollutants Analyses

Phthalates, through atmospheric transport and deposition, are found in freshwaters. These compounds are carried from the uplands of the watershed into streams and lakes during rain events. Most phthalates are used as plasticizers in the production of vinyl (PVC) to make plastics more flexible, and used in adhesives, caulking, paint pigments, nail polish and perfume. Some phthalates (such as di(2-ethylhexyl) phthalate, or DEHP) are priority atmospheric contaminants, released from industrial emissions during their manufacture (MOE 2002).

Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 different chemicals that are formed during the incomplete burning of coal, oil and gas, garbage, or other organic substances like tobacco or meat. Some PAHs are manufactured, and are found in coal tar, crude oil, creosote, roofing tar, dyes, plastics, and pesticides.

Pyrene was found at Poplar Beach at a concentration exceeding CCME's Guidelines for the Protection of Aquatic Life (CCME 2003). Like other PAHs, pyrene is ubiquitous in the environment, as it is a product of incomplete combustion and may be from a variety of industrial activities. Further study on the exact source of this compound would be difficult, because of its stability in the atmosphere and capability for long distance transport.

5.3 Recommendations

Now that baseflow inflow stream conditions have been characterized, repeated sampling should occur in the spring following run-off events. Sewage applied to land and routine dumping of lagoon wastes to creeks make spring and early summer an ideal time to monitor caffeine. As well, during the spring runoff, many more inflows contribute water to the lake, and each of these could be sampled.

Finally, if residents witness sewage dumping in unauthorized places, they should record the make and model of vehicle, license plate and physical description of the operator and immediately call Alberta Environment's 24-hour toll free reporting hotline at 1-800-222-6514.

6.0 References Cited

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7.0 Appendix A: Raw data results from ARC Vegreville