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Volume 45, No. 1, 2010

Evaluation of Risk Assessment Tools to Predict Canadian Waterborne Disease Outbreaks 1–11
I.M. Summerscales, E.A. McBean

Water Quality Effects from an Aquaculture Operation in a Meromictic Iron Pit Lake in Northwestern Ontario, Canada 13–24
K.A. McNaughton, P.F. Lee

Spatial Variability of Reproductive and Size Characteristics of the Northern Mummichog (*Fundulus heteroclitus macrolepidotus*) Collected Near Municipal Wastewater Discharges 25–34
V.A. McMullin, K.R. Munkittrick, D.A. Methven

Influences of Human Stressors on Fish-Based Metrics for Assessing River Condition in Central Alberta 35–46
C.E. Stevens, T. Council, M.G. Sullivan

Frequency Analysis as a Tool for Assessing Adverse Conditions During a Massive Fish Kill in the St. Lawrence River, Canada 47–57
V. Ouellet, M. Mingelbier, A. Saint-Hilaire, J. Morin

R.P. Rudra, B. Gharabaghi, S. Sebti, N. Gupta, A. Moharir

J. Jia, L. Thiessen, J. Schachtschneider, J. Waltho, C. Marvin

Caractérisation et traitement physico-chimique des lixiviats de la décharge publique d’El-Kerma (Algérie) par adsorption en continu sur de la sciure de bois naturelle et activée chimiquement (Characterization and physico-chemical treatment of El-Kerma (Algeria) landfill leachates by batch adsorption on untreated and chemically activated sawdust) 81–90
T. Bennama, A. Younsi, Z. Derriche, A. Debab

Research on the Application of Laccase to the Treatment of Oily Wastewater 91–98
Z.L. Li, W. Liu, X.F. Chen, H.S. Li, Y.M. Tian

Chemistry of the Interfaces of an Electric Water Heater: Implications from an Input-Output Analysis 99–109
M.B. Hocking

Philip H. Jones Award Winners iv

Instructions for Authors/Directives aux Auteurs v–xix
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PAGE LAYOUT

Lucas Neilson (Graphic Design Services, Environment Canada)

The Water Quality Research Journal of Canada
(www.wqrjc.ca)
Receives support from Environment Canada’s National Water Research Institute
(www.ec.gc.ca/inre-nwri/).
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A number of risk assessment tools and guidance documents have been developed by regulatory and nongovernmental bodies to enable risk assessment of drinking water systems. To evaluate the strengths and weaknesses of available risk assessment tools, three of the existing risk assessment tools were applied to waterborne disease outbreaks in North Battleford, Saskatchewan, and Walkerton, Ontario, to determine whether the risk assessment tools would have indicated that the water systems were at risk of failure. Both of these outbreaks are sufficiently well documented to allow testing of the risk assessment tools. Both of the outbreaks occurred partly due to vulnerabilities that prevented the respective water systems from having effective multiple barriers to drinking water contamination. The risk assessment tools generally identified the hazards that resulted in contamination of the source water. However, the different tools had different levels of success in identifying vulnerabilities in the downstream barriers such as treatment processes and water quality monitoring activities. None of the risk assessment tools successfully incorporated the interdependent nature of the multiple barriers of drinking water safety.

Key words: drinking water, risk assessment, Walkerton, North Battleford, multiple barrier approach

Introduction

A number of drinking water risk assessment tools have been developed by various regulatory agencies. Some of the tools include specific survey questions regarding water quality data, operation and maintenance practices, and the presence and robustness of barriers to prevent contamination of the drinking water supply. Basing the risk assessment and ranking process on clearly worded surveys that address water system infrastructure, operation, and performance helps to promote a thorough risk assessment process that reduces variability between users in the risk assessment output, based on their level of expertise or familiarity with the drinking water system.

For the purpose of this paper, the British Columbia Drinking Water Source-to-Tap Screening Tool (B.C. Tool) (Ministry of Health Services and Ministry of Water, Land and Air Protection 2005), the Montana Water Center Microbial Risk Assessment Ranking Tool (MRA Tool) (Montana Water Center 2010), and the risk assessment forms in the Scottish Private Water Supplies: Technical Manual (PWS) (Scottish Executive 2006) were applied to drinking water systems that have been implicated in waterborne disease outbreaks to determine whether these tools can identify the hazards and vulnerabilities that resulted in the respective outbreaks. These tools were selected because they include specific risk assessment surveys that address different aspects of the water system. Although the tools have some common survey questions, they use different scoring systems to identify and rank risks and have varying levels of involvement from regulatory authorities.

Selected Risk Assessment Tools

B.C. Tool

Under Part 3 of British Columbia’s Drinking Water Protection Act, the drinking water officer (DWO) may order a water supplier to complete a drinking water assessment if the DWO “has reason to believe that an assessment is necessary to properly identify and assess threats” to drinking water quality (Ministry of Healthy Living and Sport 2009). The B.C. Tool represents the
first tier of the assessment process (Ministry of Health Services and Ministry of Water, Land and Air Protection 2005). The B.C. Tool is used to compile information regarding the operation and management of the water system, the quality of tap water supplied by the system, the water system infrastructure, and chemical and microbial hazards that could enter the water supply. The B.C. Tool is completed by the water supplier and submitted to the DWO for review (Ministry of Health Services and Ministry of Water, Land and Air Protection 2005). In the event that the DWO feels that potentially significant risks have been identified based on the input to the B.C. Tool, the DWO may issue an order for the supplier to complete selected modules of the B.C. comprehensive drinking water source-to-tap assessment process (source-to-tap assessment process) in order to further investigate and assess the identified risks. The modules are completed by a multidisciplinary team of qualified professionals with experience relevant to drinking water systems (Ministry of Health Services and Ministry of Water, Land and Air Protection 2005). The hazards identified when completing any of modules 1 through 6 are then ranked using a qualitative risk assessment procedure as part of module 7. A flowchart of the source-to-tap assessment process is included as Fig. 1.

For the purpose of this study, it was assumed that a qualified DWO would have an undergraduate degree in science or engineering, several years of professional experience in the drinking water field, and would have completed any necessary job-specific training programs with respect to the source-to-tap assessment process. It stands to reason that if the DWO orders the water supplier to complete a risk assessment module addressing a particular aspect of the drinking water system based on the input to the B.C. Tool, the assessment team would identify the hazards and vulnerabilities associated with that aspect of the system when completing the module. If for some reason the DWO did not have sufficient experience with small drinking water systems or the necessary training with respect to the source-to-tap assessment process to identify a potential hazard or vulnerability based on the input to the B.C. Tool, then the DWO would be less likely to order the supplier to complete the risk assessment module relevant to that hazard or vulnerability. As a result, the risk assessment team would be more likely to overlook that hazard or vulnerability when completing the modules included.

**Fig. 1.** British Columbia comprehensive source-to-tap risk assessment flowchart.
in the order, which would limit the effectiveness of the source-to-tap assessment process.

In this manner, the ability of a qualified DWO to identify hazards and vulnerabilities based on the input to the B.C. Tool was used to determine whether the source-to-tap assessment process would identify the factors that led to the waterborne disease outbreaks in North Battleford and Walkerton.

**MRA Tool**

The MRA Tool is available from the Montana Water Center at Montana State University and the National Environmental Science Center at West Virginia University (Montana Water Center 2010). The MRA Tool is meant to assist small water system operators and managers in identifying potential microbial risks and corrective actions that can be taken to manage those risks. Using the MRA Tool does not eliminate the need for a sanitary survey or vulnerability assessment of the water system (Butterfield and Camper 2004).

The MRA Tool is available as a Microsoft Excel spreadsheet. The MRA Tool includes a number of different survey forms specifically tailored to alternative water supplies (i.e., streams and rivers, lakes and impoundments, wells, or springs) and treatment systems (i.e., treatment of groundwater or surface water), as well as survey forms addressing other water system infrastructure and water quality monitoring activities (Butterfield and Camper 2004). A flowchart for the MRA Tool is included as Fig. 2.

Based on the input from the operator, each survey question receives a numerical risk score ranging from 0 to 1 (Butterfield and Camper 2004). The MRA Tool provides comments and recommendations regarding measures that can be taken to reduce the risk associated with survey questions that receive high relative risk scores. The relative risk scores associated with each question for a particular survey are weighted and summed to calculate a total microbial risk score for the survey, which is also in the range of 0 to 1. The risk scores for all surveys are then weighted and summed again to determine the overall risk score for the water system (Butterfield and Camper 2004).

The weights assigned to the survey questions were calculated using the ranked pairwise comparison method (Saaty 1980). The version of the MRA Tool that is available to the public does not list the weights, nor does it allow the user to access the matrices used to calculate the weights. If the user does not agree with relative risk scores assigned to the individual survey questions, the user can request access to the Excel spreadsheet that was used to calculate the weights from the developers of the MRA Tool. The weights can then be adjusted by having an expert complete the pairwise comparison matrices (Butterfield and Camper 2004). Since the MRA Tool is

**Fig 2. MRA tool schematic.**
meant to be used by the owner or operator of a small water system, and small water system personnel are unlikely to have the necessary risk assessment expertise to make accurate revisions to the weights (Butterfield and Camper 2004), the default weights were not adjusted for the purpose of this study.

The inquiry reports and other literature published regarding the waterborne disease outbreaks generally focused on the hazards or vulnerabilities of the water systems that led to the waterborne disease outbreaks. As a result, the authors made assumptions that they felt were reasonable in order to complete the survey forms for water system components that were not implicated in the outbreaks. The risk scores associated with the different components of the water system were then compared to determine if the MRA Tool correctly identified the aspects of the water system that contributed to the waterborne disease outbreak.

PWS Risk Assessment Forms

This risk assessment process is completed by the local authority with input and assistance from the “Relevant Persons” responsible for the water supply (Scottish Executive 2006). An assessment is completed when a new water supply is brought into service, an existing supply is returned to service after being out of use for a period of greater than one year, or if the local authority has reason to believe the water supply is no longer “wholesome” (The Scottish Ministers 2006).

The PWS includes separate risk assessment forms for different water supplies (surface water supplies, springs, wells, and boreholes). Each risk assessment form has common sections that collect information regarding relevant contact information, historic water quality data, and the results of past risk assessments. The inspector must also complete a process flow diagram for the water system in this section. The information required to complete the General Site Survey, Supply Survey, and Soil Leaching Risk Survey (for springs and wells only), varies depending on the type of water supply (Scottish Executive 2006). Since neither of the water systems reviewed in this paper were supplied by springs or wells (i.e., dug or sand point wells), the Soil Leaching Risk Survey could not be assessed.

Each survey has two scores associated with it: the risk characterization and the hazard assessment scores (Scottish Executive 2006). Qualitative risk characterization scores are assigned to survey questions regarding the presence or absence of hazards and vulnerabilities that could have an impact on water quality. For each survey question, the user must answer “yes,” “no,” or “don’t know.” One of three risk characterization scores (high, medium, or low) is preselected for each of the potential answers. The highest risk characterization score for a survey question is recorded as the risk characterization score for that survey (Scottish Executive 2006).

The hazard assessment score uses a semiquantitative risk assessment procedure (Scottish Executive 2006). The user selects a likelihood score based on a five-point nonordinal scale, where a score of 1 represents a hazard that is rarely present and a score of 16 represents a daily or permanent hazard. The severity is scored based on the same five-point nonordinal scale, and is preselected on the survey form for each question. The likelihood and severity scores are multiplied to determine the hazard assessment score, which is considered to be “an index with no implied mathematical relationship to risk” (Scottish Executive 2006). The maximum hazard assessment score is 256; the PWS recommends that a threshold score of 16 be used to prioritize hazards for corrective action (Scottish Executive 2006). A flowchart for the completion of one of the survey questions listed in a PWS risk assessment form is included as Fig. 3.

Completing the General Site Survey and the Supply Survey for this tool requires a detailed survey of potential chemical and microbial hazards in the vicinity of the source, as well as vulnerabilities present based on the current condition of the source and other water system infrastructure. Since all of the survey questions could not be accurately answered based on published information for the selected case studies, the authors made assumptions that they felt were reasonable in order to complete the survey forms. In the event that the MRA Tool and PWS risk assessment forms included similar questions that could not be answered based on published information, the same assumption was made when completing both risk assessment tools.

Case Studies

North Battleford, Saskatchewan

Background. The City of North Battleford is located on the north banks of the North Saskatchewan River, approximately 140 km northwest of the City of Saskatoon. At the time of the outbreak, the City had a population of approximately 15,000 (Hrudey and Hrudey 2004).

The North Battleford distribution system is served by two water treatment plants, a groundwater treatment plant (GWTP) and a surface water treatment plant (SWTP). Since the GWTP was not implicated in the outbreak, it will not be discussed further.

The SWTP receives raw water from a surface water intake located in the North Saskatchewan River. According to the North Battleford Water Inquiry, the SWTP did not operate continuously, but provided supplemental flow to the GWTP (Laing 2002). At the time of the outbreak, water treatment chemicals added prior to the solids contact unit (SCU) included coagulants, oxidizing agents to oxidize organic compounds that can cause taste and odour issues, and chlorine to achieve primary disinfection. No rapid mixing was provided prior to water entering the SCU to promote coagulation or mixing of the disinfectant and the raw water. In the SCU, a polymer was added to assist with flocculation, and lime was added to adjust the pH. The effluent from the SCU was directed to one of two sets of two multimedia
filters piped in parallel. The effluent from the filters then entered the clear wells (Laing 2002).

According to the North Battleford Water Inquiry, the SWTP was shut down in order to repair a crack in the floor of the SCU on March 20, 2001. The SCU was completely drained such that there was no remaining sludge blanket. When repairs were completed, the SWTP was returned to service after a relatively short commissioning period, despite the fact that negligible settling was being achieved in the SCU (Laing 2002). The poor performance of the SCU resulted in the multimedia filters being backwashed on a more frequent basis. Since filters No. 3 and No. 4 were not designed with “filter-to-waste” capabilities, and the SWTP operators were not in the practice of directing effluent from filters No. 1 and No. 2 to waste after a backwash cycle was completed (Hrudey and Hrudey 2004), water that had undergone minimal solids removal entered the clear wells and was eventually pumped to the distribution system. The SCU continued to achieve negligible settling until April 24, 2001. Due to evidence of gastroenteritis in the community and the poor settling in the SCU, a Precautionary Drinking Water Advisory (PDWA) was issued on April 25, 2001, and was upgraded to a boil water order the following day. The boil water order remained in effect until July 25, 2001 (Laing 2002).

The first confirmed case of cryptosporidiosis was identified on April 4, 2001 (Laing 2002); a total of 275 cases were confirmed for residents and visitors to the City by May 2001 (Stirling et al. 2001). An estimated 5,800 to 7,100 area residents suffered from gastroenteritis between March 20 and April 26, 2001 (Laing 2002).

**Results for B.C. Tool.** Based on the input to the B.C. Tool, a number of hazards were identified that could impact the water quality in the North Saskatchewan River. Although little information was available regarding potential sources of contamination within 50 m of the surface water intake, a number of sources were identified within the watershed. Livestock operations and municipal wastewater treatment plant (WWTP) operations are two activities present in the watershed that represent potential sources of *Cryptosporidium* oocysts (Laing 2002).

To complete the treatment survey of the B.C. Tool, the water supplier would have indicated that treatment at the SWTP consisted of the addition of chlorine to achieve primary disinfection, the SCU (which generally provided coagulation, flocculation, and sedimentation), and then filtration. Based on this limited information, the DWO would have likely concluded that the SWTP was capable of treating a surface water source, despite the lack of alarms for chlorine dosing and monitoring equipment.
However, information collected in other sections of the B.C. Tool regarding historical water quality issues, including a previous PDWA due to total coliform counts and low free chlorine levels in the distribution system in September 2000 (Laing 2002), would have suggested that the SWTP was probably not achieving optimal performance. As a result, it is likely that the DWO would order the water supplier to perform an assessment of water system infrastructure (Module No. 3), which would have identified vulnerabilities in the design of the SCU, filters, and chlorination equipment. In addition, the order would likely also require the owner to complete the following modules:

- Module 1, which would have demonstrated the highly variable levels of turbidity and Cryptosporidium oocysts in the raw water supply (Laing 2002), assuming that the assessment team requested relevant monitoring data collected by larger upstream municipalities;
- Module 2, which would have identified sources of microbial contamination in the watershed;
- Module 5, which would have identified historical trends in raw, treated, and distribution water quality, and the effect that variations in raw water quality and treatment performance have had on distribution water quality in the past.

Modules 7 and 8 would be completed based on the identified hazards and vulnerabilities. By completing these modules, the risk assessment team would have identified the hazards and vulnerabilities associated with the surface water source and SWTP that led to the waterborne disease outbreak in North Battleford. However, the time and resources required to complete the process, from the submission of the screening tool by the water supplier through to the completion of the qualitative risk assessment and risk assessment identification modules, would not result in the hazards and vulnerabilities being addressed promptly.

**Results for MRA Tool.** Since the GWTP was not implicated in the outbreak, the MRA Tool surveys that address the groundwater wells and GWTP infrastructure were not completed. Based on the information input to the MRA tool spreadsheet, the North Battleford water system received a relatively high overall risk score of 0.537. The components of the water system that made the greatest contribution to the overall risk score were the surface water (SW) source (0.214, 39% of the overall score), the SWTP (0.143, 26% of the overall score), and the distribution system (0.074, 14% of the overall score).

The SW survey question that received by far the highest risk score addressed upstream wastewater discharges. The risk score assigned to this question was approximately twice that of the second-highest risk score, which was assigned to the question regarding upstream stormwater discharges. The survey question regarding stormwater discharges addresses potential discharges from livestock activities as well as from urban areas. The SW survey identified and assigned significant risk scores to the two hazards in the watershed that are most likely to have resulted in *Cryptosporidium* oocysts entering the North Saskatchewan River.

The two SWTP survey questions that received the highest risk scores address the percent of time that the SWTP met treatment requirements with respect to CT limits—where CT is calculated by multiplying the effluent residual disinfectant concentration in milligrams per litre by contact time in minutes—and turbidity limits, respectively. It was assumed that each of these limits was met 90% of the time, which may in fact be an underestimate that would result in artificially high risk scores for these questions. It is also worth noting that these questions do not address hazards or vulnerabilities associated with the operation of the SWTP directly, but are based on available monitoring data. Typically, one would expect this information to be used as a line of evidence in the risk assessment process instead of it receiving a risk score directly. The SWTP survey question that received the third highest risk score addresses the lack of alarms associated with the disinfection system. Connecting the gas chlorination system and the clear well chlorine monitoring equipment to an alarm system would alert operators when the disinfection equipment failed or water entered the clear wells with a low chlorine residual. While this would not have prevented the waterborne disease outbreak in North Battleford, it would help promote adequate inactivation of other pathogens, such as *Giardia* cysts and viruses, in the clear wells.

The MRA Tool requires far more information regarding the design of the treatment system than the other two risk assessment tools that were evaluated as part of this study. As a result, the MRA treatment survey identified design flaws in the SWTP, including the absence of rapid mixing prior to water entering the SCU and the inability to filter-to-waste prior to returning the multimedia filters to service after a backwash cycle. However, the risk scores assigned to these survey questions were relatively low, so it is highly unlikely that they would be identified as areas where remedial action was necessary based on the results from the MRA Tool.

While the SWTP survey identified issues with the performance and the design of the SWTP, it did not identify the operating decisions that led to the cryptosporidiosis outbreak. It would require a significant increase in the number of survey questions regarding plant operations in order to determine that sludge was completely drained from the SCU in order to complete repairs, and that there was poor settling in the SCU when it was returned to service. Further increasing the number of survey questions would increase the effort required to complete the tool, making it less user-friendly. A more effective solution might be to modify the tool to focus on the design of the SWTP and the lack of multiple barriers with respect to *Cryptosporidium* removal or the lack.
of redundancy with respect to the SCU. The presence of multiple barriers that are capable of removing or inactivating pathogens is particularly important for raw water sources that contain Cryptosporidium (Jameson et al. 2008). This would allow the MRA Tool to better represent the integrated nature of the multiple barrier approach to drinking water safety.

The highest risk score for the distribution survey was assigned to the question regarding dead ends and low flow areas in the distribution system. The risk score was not based on the presence of these low flow areas so much as the results of recent sampling activities performed in these areas, such as the positive total coliform and low residual chlorine results that led to the September 2000 PDWA (Laing 2002). The other survey question to receive a relatively high risk score addresses residual disinfection and whether the free chlorine concentration drops below 0.2 mg/L in the distribution system. As a result, the low residual disinfectant concentrations in the distribution system is identified twice in the distribution survey, making the risk score for the distribution system highly dependent on water quality monitoring results. While the presence of coliform bacteria or low chlorine residuals does indicate a water quality problem, it does not help to identify the source of that problem.

**Results for PWS surface water risk assessment form.**

Although the risk characterization and hazard assessment scores for the water system are based on the information input in the General Site Survey and Supply Survey, information that is relevant to the risk assessment process is also collected in the “front end” of the risk assessment forms. The question regarding water quality results for the previous 12 months would bring the September 2000 PDWA to the attention of the inspector.

For the purpose of evaluating the risk assessment form, it was assumed that any activity that is known or assumed to occur in the North Saskatchewan River watershed could impact water quality at the intake. As a result, survey questions regarding the following hazards were assigned high risk characterization scores:

- Livestock production, which would be a permanent feature due to the presence of cattle operations in the watershed;
- Surface runoff from agricultural activities, which was assumed to occur during storm events and snowmelt;
- Land application of manure, which was likely to occur based on the cattle operations present in the watershed;
- Sewer lines and the WWTP discharge, which was located approximately 3.5 km upstream of the SWTP intake (Laing 2002).

Both the livestock production and WWTP discharge questions received the maximum hazard assessment score of 256. The activities in the watershed that represent the likely source of Cryptosporidium oocysts in the North Saskatchewan River were identified and received high hazard assessment scores.

The questions in the Supply Survey were applied to all infrastructure associated with the SWTP and distribution system. The survey question regarding the integrity of piping material received a high risk characterization score because the majority of the distribution system piping was constructed of asbestos cement (MR2-McDonald and Associates 2006). The PWS specifically identifies asbestos concrete as a piping material that is likely to fracture or deteriorate (Scottish Executive 2006). The two other survey questions that received high risk characterization scores addressed fluctuations in the flow and quality of the source water. Based on these results, the PWS surface water risk assessment form does not address water treatment or operational practises in sufficient depth to identify the vulnerabilities in the SWTP.

**Walkerton, Ontario**

**Background.** Walkerton is a rural community located in Bruce County, Ontario. At the time of the outbreak, the town had a population of approximately 4,800 (Hrudey and Hrudey 2004).

At the time of the outbreak, the Walkerton municipal drinking water system was supplied with water by three drilled wells: Wells No. 5, No. 6, and No. 7. Based on the Report of the Walkerton Inquiry, each well was completed in an unconfined fractured bedrock aquifer (O’Connor 2002). Well No. 5 was completed at a shallow depth of 15 m; Well No. 6 and Well No. 7 were significantly deeper (72.2 and 76.2 m, respectively). Each well was outfitted with a separate chlorination system to achieve primary disinfection prior to the treated water reaching the nearest consumer (O’Connor 2002).

According to the Report of the Walkerton Inquiry, the accumulated rainfall for the Walkerton area over the period of May 8 to 12, 2000 was 134 mm, which was equivalent to a 60-year storm event for this area in the month of May (O’Connor 2002). Flooding occurred in the town and in the area of Well No. 5. On May 9, 2000, the water supply was switched from Well No. 7 (which was in operation despite not having a functioning chlorination system at that time) to Wells No. 5 and No. 6. Well No. 5 operated continuously and was the primary water source from May 10 until the afternoon of May 15, with the exception of a period of approximately 16 hours between the evening of May 12 and the afternoon of May 13 when it was shut down (O’Connor 2002). Since Wells No. 6 and No. 7 were not implicated in the outbreak, they will not be discussed further.

According to the Report of the Walkerton Inquiry, Walkerton Public Utilities Commission (PUC) staff recorded free chlorine residual concentrations of 0.75 mg/L for treated water from Well No. 5 on May 13, 14, and 15. It is unlikely that the recorded numbers were accurate, as PUC staff often falsified records with respect to free chlorine levels (O’Connor 2002). On May 15, PUC staff collected several water samples, a number of which may have been labelled with the incorrect
sampling location (O’Connor 2002), and shipped them to a private laboratory for microbiological analysis. On May 17, the PUC was notified that the majority of these samples were positive for both Escherichia coli and total coliform bacteria. PUC staff increased chlorine feed rates and began flushing the distribution system on May 19, 2000. PUC staff withheld the adverse water quality results from the Ontario Ministry of the Environment and Bruce-Grey-Owen Sound Health Unit (PHU) staff until May 22, 2000 (O’Connor 2002).

The first confirmed case of E. coli was identified on May 21, 2000. Based on this case and a stool sample from another patient that was presumptive positive for E. coli, the PHU issued a boil water advisory on the afternoon of May 21. The outbreak resulted in an estimated 2,321 cases of illness (O’Connor 2002), 167 confirmed cases of E. coli O157:H7, 116 confirmed cases of Campylobacter (Bruce-Grey-Owen Sound Health Unit 2000), 27 cases of Hemolytic Uremic Syndrome due to exposure to E. coli O157:H7, and 7 deaths (O’Connor 2002).

Results for B.C. Tool. Well No. 5 was correctly identified as being vulnerable as it is a shallow well that draws water from an unconfined fractured bedrock aquifer, and was located within 30 m of two springs (O’Connor 2002). The B.C. Tool also identified manure storage and application (activities thought to be responsible for the contamination of the water supply; O’Connor 2002) and improperly abandoned wells (Howard 2006) as potential sources of contamination located within 300 m of Well No. 5.

The only issue that was identified with respect to treatment was that the chlorination and disinfection monitoring equipment were not connected to alarms. Although chlorination was the only form of treatment at each well, it is generally thought to be sufficient for disinfection of a secure groundwater source. However, based on the input to the B.C. Tool regarding Well No. 5, the raw water supply would not be considered secure. In addition, information collected in other sections of the B.C. Tool regarding historical water quality issues, including raw and distribution samples that exceeded Guidelines for Canadian Drinking Water Quality limits for E. coli and total coliform bacteria (O’Connor 2002), would indicate that the chlorination equipment may not be achieving primary disinfection.

As a result, the DWO would likely have ordered the water supplier to complete the following modules:

- Module 1, which would have shown that the aquifer Well No. 5 draws from is vulnerable based on its geology and historic raw water quality data;
- Module 2, which would have identified sources of microbial contamination in the capture zone, and natural and man-made vulnerabilities that could act as conduits to the aquifer;
- Module 3, which would have likely shown that the treatment equipment installed at Well No. 5 was not sufficient to treat a vulnerable groundwater source;
- Module 5, which may not have effectively identified trends in raw or treated water quality due to the aforementioned PUC practise of mislabelling water samples.

By completing these modules, the risk assessment team would likely have identified all of the hazards and vulnerabilities associated with Well No. 5 and its treatment system that led to the waterborne disease outbreak in Walkerton. However, the time and resources required to complete the process, from the submission of the screening tool by the water supplier through to the completion of the qualitative risk assessment and risk assessment identification modules, would not allow for the hazards and vulnerabilities to be addressed promptly.

Results for MRA Tool. Since Wells No. 6 and No. 7 were not implicated in the outbreak, surveys were not completed for these wells or their treatment systems. Based on the information input to the MRA tool, the Walkerton water system received an overall risk score of 0.537. The surveys that made the largest contributions to the overall risk score are the treatment survey (0.137, 26% of the overall risk score), the source survey (0.128, 24% of the overall risk score), and the distribution survey (0.110, 20% of the overall risk score).

Due to the periodic positive coliform results in the four-year period preceding the outbreak (O’Connor 2002), the source survey question regarding historical microbial contamination received the highest relative risk score. The second highest risk score for the source survey was assigned to the question regarding aquifer type. Based on information regarding the geologic formation that the well was completed in, and the fluctuations in water level and water quality observed at Well No. 5 (O’Connor 2002), the well was in need of a groundwater under the direct influence of surface water (GUDI) assessment at the time of the contamination event. The need for a GUDI assessment results in a significant increase in the relative risk score assigned to the survey question regarding the aquifer type compared with a non-GUDI well. As a result, the source survey identifies one of the vulnerabilities that contributed to the waterborne disease outbreak.

The third and fourth highest risk scores for the source survey were assigned to questions regarding the completion of a source water assessment and source water protection plan. While preparing these documents would help identify the hazards or vulnerabilities that were present, the survey questions themselves do not address hazards or vulnerabilities directly. The same issue exists with the survey question regarding historical microbial contamination, which determines whether there is recent evidence of contamination, but does not identify the source of the contamination. As a result, the risk scores assigned to survey questions addressing actual hazards (such as livestock activities in the area of influence) and vulnerabilities (such as the shallow static water depth and relatively short well casing depth of Well No. 5) are
eclipsed by the relatively high risk scores assigned to survey questions that address lines of evidence.

The survey question regarding corrosion control made the greatest contribution to the total risk score for the treatment survey. Since the survey question does not account for the physicochemical characteristics of the raw water supply or the pipe materials used in the transmission mains and the distribution system, the MRA Tool may not accurately reflect the microbial contamination risk associated with corrosion. The second highest risk score was assigned to the survey question regarding monitoring alarms for disinfection equipment. If continuous free chlorine monitoring equipment was installed and connected to an alarm system at Well No. 5, PUC operators would have been notified when insufficiently treated water entered the distribution system. This could have drastically reduced the scope of the outbreak (O’Connor 2002), provided that PUC operators took appropriate action to address the problem. Similarly, installing continuous turbidity monitoring equipment and connecting it to an alarm system may have notified the operator when contaminated water entered the distribution system. Despite that fact, the lack of turbidity monitoring alarms makes a relatively small contribution to the total risk score for the treatment survey. A relatively low weight may have been assigned to this survey question because turbidity monitoring is generally not required for secure groundwater sources. However, the user input to the source survey indicated that a GUDI assessment was required for Well No. 5. The need for a GUDI assessment increased the risk score assigned to the question regarding the aquifer type in the source survey, but it did not have an impact on the risk score calculated for the GWTP despite the fact that GUDI sources generally have more stringent treatment and monitoring requirements.

The treatment survey question regarding the residual chlorine concentration after treatment, which was assumed to be in the range of 0.2 to 0.5 mg/L based on evidence presented at the Walkerton Inquiry (O’Connor 2002), also received a relatively high risk score. Unlike the SWTP survey, the GWTP survey does not include a question regarding the percent of time that the treatment facility meets CT requirements, only a question to determine whether the equipment has sufficient capacity to meet the CT requirements at all flow rates. A question should be included in the treatment survey to determine whether the necessary CT level is consistently being achieved, as CT values are directly correlated to the log inactivation achieved for a given disinfectant and pathogen (Hrudey and Hrudey 2004). If the treatment equipment has the capacity to meet CT requirements, but the CT requirements are not being met on a consistent basis, then the need for improved operating and monitoring practises would be identified. Poor operating and monitoring practises were identified as one of the factors contributing to the Walkerton outbreak (O’Connor 2002). In summary, a number of treatment survey questions identified factors that allowed contamination to enter the distribution system in Walkerton, but the MRA Tool did not assign the highest risk score to those survey questions.

In the distribution survey, the question regarding distribution system repairs and the required commissioning activities (flushing, disinfection, and bacteriological sampling) received the highest relative risk score. The high score was assigned because the work was performed by outside contractors. If water system operators performed the work, the risk score assigned to the question would be zero. Based on the poor operations and maintenance practises of Walkerton PUC staff, one would expect that properly trained private contractors would be more likely to follow the necessary safety and disinfection procedures when completing distribution system repairs. The risk scoring for this question, as well as for other survey questions regarding distribution system construction and maintenance activities, suggests that there is less risk associated with these activities when they are performed by water system personnel. This may not be a valid assumption for small water systems where operators are less likely to have the necessary equipment and training to perform this work in a safe manner.

Similar to the results for the North Battleford water system, distribution survey questions regarding dead end and low flow areas and residual disinfection also received relatively high risk scores. Due to the PUC practise of maintaining low chlorine doses (O’Connor 2002), the low chlorine residual in the distribution system may be due to the low chlorine concentration in treated water as it entered the distribution system.

Results for PWS borehole risk assessment form. The front end of the risk assessment form would bring recent adverse water quality results to the attention of the inspector. Three of four raw water samples collected from Well No. 5 in April 2000 tested positive for total coliform bacteria, as did two treated water samples collected for the Well No. 5 treatment system on April 3 and April 17 and two distribution samples collected on April 3 (O’Connor 2002). For the purpose of the survey question regarding stagnant or standing water, it was assumed that the springs located near Well No. 5 qualified as “standing water.” Well No. 5 received a high risk characterization score for this question as well as for other General Site Survey questions regarding manure application activities and out-of-use wells. These questions identified the source of contamination responsible for the outbreak, and potential routes for that contamination to enter the supply aquifer.

The questions from the Supply Survey were applied to all infrastructure associated with the Walkerton water system. There is no indication that a suitable physical barrier was in place to prevent Well No. 5 from being flooded. As a result, a high risk characterization score and the maximum hazard assessment score were assigned to
this survey question. Survey questions regarding fluctuations in the well water level and raw water turbidity at Well No. 5 also received high risk characterization scores. Fluctuations in water level and turbidity were recorded in inspection reports completed by Ontario Ministry of the Environment environmental officers over the period of 1978 to 1980 (O’Connor 2002). Other Supply Survey questions regarding the water system infrastructure, specifically the number of unprotected cross-connections in the distribution system (Ministry of the Environment 2000) and the lack of maintenance activities performed in the previous year (O’Connor 2002), also received high risk characterization scores. In summary, the PWS borehole risk assessment form identified the hazards and vulnerabilities that led to the contamination of Well No. 5, but did not address water treatment or monitoring activities in sufficient depth to identify vulnerabilities in the chlorination system.

Conclusions

Each of the selected risk assessment tools successfully identified the hazards that led to contamination of the water source in both case studies. However, the tools have different levels of success when identifying vulnerabilities associated with the water source and treatment, and water quality monitoring activities.

Although the B.C. Tool did not successfully identify vulnerabilities associated with water treatment directly, in both cases the DWO would have ordered the water supplier to complete the source-to-tap assessment modules necessary to identify the risks that led to the outbreaks based on the input to the B.C. Tool. The concern with the tiered approach of the source-to-tap assessment process is that it would be too onerous for a small water system operator to complete in a reasonable amount of time.

Alternatively, the MRA Tool is a single-tier risk assessment tool that requires more information regarding the design of the water treatment system than the B.C. Tool. However, the relatively high risk scores assigned to questions regarding historical treated water quality monitoring data can eclipse the risk scores associated with the vulnerabilities in the treatment system that led to the outbreak, which may decrease the likelihood that the water supplier will take direct action to address these vulnerabilities.

The PWS risk assessment forms do not include questions regarding water treatment or monitoring equipment, with the exception of two questions addressing a point-of-entry or point-of-use treatment system. These questions are designed for very small water systems, and are generally not applicable to larger water systems that serve residential or mixed-use developments.

The major shortcoming for all of the selected risk assessment tools is that they do not reflect the interdependent nature of the barriers to drinking water contamination. The survey questions addressing the source, treatment, and distribution of the water system are considered in isolation from one another. If the water system barriers were properly integrated in a risk assessment tool, the vulnerability of Well No. 5 to surface water contamination would result in an increase in the weightings or risk scores being assigned to survey questions regarding downstream treatment and monitoring barriers. The presence of alarmed continuous monitoring equipment would have likely prevented the Walkerton outbreak.

The three risk assessment tools also fail to address redundancy of key equipment or processes capable of removing pathogens. The installation of parallel “stand by” equipment can help to ensure that high quality water is supplied to the user in the event of equipment breakdown or scheduled maintenance. For example, the installation of a second SCU in parallel with the duty unit at the North Battleford SWTP would have provided the water system operators with sufficient time and operational flexibility to ensure that the duty SCU was achieving adequate settling prior to returning it to service, which would have likely prevented the North Battleford outbreak.

Recommendations

The development of future risk assessment tools must account for the interdependent nature of the barriers to drinking water contamination, as this important concept is not adequately addressed by the existing risk assessment tools assessed herein. Vulnerabilities in an upstream barrier would have an impact on the weights or risk scores assigned to survey questions regarding relevant downstream barriers. Elevated weights or risk scores would be assigned to survey questions regarding a hazard when there is only one process or barrier capable of removing or inactivating it. Future risk assessment tools must also incorporate the importance of redundancy within individual water system barriers, such that an elevated risk score is assigned if there is no “stand by” equipment that can be brought into service in the event that the process fails.

Acknowledgments

This research was made possible due to funding from the Canadian Water Network and Natural Science and Engineering Research Council of Canada Discovery grants. Stewart Schafer, the Director of Public Works and Engineering for the City of North Battleford, is also acknowledged for providing access to information regarding the condition of the water system at the time of the waterborne disease outbreak.

Abbreviations/Acronyms

B.C. Tool: British Columbia Drinking Water Source-to-Tap Screening Tool
CT: Effluent residual disinfectant concentration in milligrams per litre multiplied by contact time in minutes
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Received: 30 March 2009; accepted: 15 December 2009.
Water Quality Effects from an Aquaculture Operation in a Meromictic Iron Pit Lake in Northwestern Ontario, Canada

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In 1989, aquaculture for the production of rainbow trout (*Oncorhynchus mykiss*) was started in the upper depths of the 180-m deep Caland pit lake formed after the flooding of the former Steeprock Iron Mine. After ten years of operation, water quality was shown to be affected by the fish farm as well as proximal waste and the surficial geology of the area. Meromictic conditions occurred in the pit lake with a dichotomy in water quality versus depth. A cluster of parameters (ammonia, total phosphorus, total Kjeldahl nitrogen, dissolved organic carbon, B, pH, dissolved oxygen) were either in higher concentrations in the mixolimnion or varied little throughout the entire water column, and a second cluster of parameters had higher levels below the chemocline (conductivity, alkalinity, dissolved inorganic carbon, total dissolved solids, nitrate, sulfate, Ca, Mg, hardness, Na, Cl, K, Fe, Mn, Sr, and silicon dioxide). Statistically significant variations in concentrations among many of these chemical parameters were observed between the two years of study, among depths, and among seasons. Nutrient loading from excess fish food and waste increased phosphorus and ammonia levels. The expansion of the fish farm also reduced the levels of dissolved oxygen in the lower depths of the pit lake, thus reducing the volume of usable water for aquaculture purposes. In the early 2000s the fish farm decreased production and those closed in 2006. Later data showed that nitrate and potassium had corresponding decreases in both the monimolimnion and the mixolimnion. Sulfate levels remained elevated.

Key words: pit lake, aquaculture, meromictic, northwestern Ontario

Introduction

The closure of open pit mines and their subsequent filling with both ground and surface waters has produced many pit lakes (Miller et al. 1996; Banks et al. 1997; Doyle and Runnells 1997). These pit lakes differ from natural lakes. They are usually very deep, have low surface to depth ratios, often lack any outflow to the surrounding watershed, and in addition to thermal stratification, often have chemical stratification caused by runoff from the newly scoured surfaces of the open pit operations (Hamblin et al. 1997).

It has been suggested that if there is sufficient acid-buffering capacity, these closed lake systems could be used for aquaculture as an alternative approach to conventional mine closure rehabilitation. In northern Minnesota and in northern Quebec, aquaculture operations were established in several abandoned open pits that had moderately hard water (Cornel and Whoriskey, 1993; Axler et al. 1996). Unfortunately the development of anoxic conditions in the hypolimnion, as chemical and microbial oxidation of fish food and feces occurs, may result in eutrophic conditions and adversely affect the water quality of the receiving water body (Axler et al. 1992). Nevertheless, the premise of utilizing an abandoned mine site for aquaculture remains attractive from both an economic and social sense.

If such pit lakes are to be used for aquaculture, it is necessary to identify the potential impact of these operations on the environment and develop techniques that can minimize or remediate any problems. The first step in this process, and the objective of this study, is to separate the impacts of the aquaculture operation on water quality from those occurring from the weathering of exposed mine rock and tailings.

Methods

Study Site

The study site consists of flooded open pits located in the former middle and east arms of Steep Rock Lake (48°48’N, 91°39’W) near Atikokan, Ontario, Canada (Fig. 1). The largest pits are Hogarth in the middle arm and Caland pit lake in the east arm. These sections of Steeprock Lake were isolated from the main lake in the early 1940s by a series of diversions and dams. The area was drained, its overburden removed, and the ore extracted. Mining occurred from 1944 to 1979. After mining ceased, the pits began to fill with water from rainfall, runoff, and groundwater seepage from their drainage basin which encompasses an area of 16.8 km². As the basin fills, the pits will eventually join and reach depths greater than 300 m before discharging into the west arm of Steeprock Lake and from there into the Seine River.

The Steep Rock area contains Archean metavolcanic, metasedimentary, and intrusive rocks which have been displaced by a series of faults (Shklanka 1972). These rocks lie on weathered granite rocks which separate the main sections of the ore body.

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The ore is bordered by “paint rock,” a soft clay-like material eroded from the limestone, and by “ash rock” formed from volcanic ash. A footwall carbonate formation, which varies in composition from calcite (CaCO₃) to dolomite (CaCO₃·MgCO₃), underlies the paint rock. There are also small patches of conglomerates made up of Archean sand and gravel deposited by an ancient sea (Pye 1968). The displacement of the granitic masses along the faults caused folding and tilted the ore body and associated rocks to a near vertical position. The ore extended to a depth of 760 m, width of 50 m, and length of over 4 km. The ore consisted mostly of goethite and hematite and averaged 56.5% Fe, 3.42% Si, 0.17% P, 8% Al, and 0.21% Mn (Steep Rock Mines 1943). Although it is possible the iron originated from volcanic exhalations, the most accepted theory for iron deposition in the region is that the iron was precipitated as oxides in the shallow waters of a Precambrian sea in limited areas where oxygen became abundant in the water column (Cloud 1973; Ojakangas and Marsch 1982). The occurrence of large fossilized blue-green algal mounds at the Hogarth pit gives credence to this hypothesis.

The present study is concerned with Caland pit lake. By 1999, the depth and area of Caland pit lake were approximately 180 m and 120 ha, respectively. The pit lake is steep sided and well sheltered from winds.

Snow Lake Fish Farm commenced cage culture with chinook salmon (Oncorhynchus tsawytscha) in 1989 in Caland pit lake. By 1992 salmon production reached 91,000 kg total weight, but was discontinued since food conversion was inefficient. In 1993 rainbow trout (Oncorhynchus mykiss) production expanded, reaching 57,000 kg by 1995. In 1996, because of damage to the farm from ice and storms, rainbow trout production decreased to 36,000 kg. In 1997 production further declined to 20,000 kg. In 1998 a major expansion of the facility was undertaken, and by the end of the year there were 450,453 fish with a biomass of 84,629 kg. In December 1999 fish numbers averaged 733,325 with a biomass 163,325 kg, and by August 2000 production reached 227,000 kg. With increases in fish, the amount of fish food utilized also increased from 146,000 kg in 1998 to 214,000 kg in 1999.

Field Procedures

Figure 1 shows the locations of the three sampling stations in the pit lake and the four drainage sampling stations. The three sampling stations were the same as those used by the Ontario Ministry of the Environment in 1992.

In the first year, sampling was conducted monthly from June to September, 1998, before ice cover in early November and after ice cover in late February 1999, for a total of six times. In the second year, the same sampling regime was followed except it started immediately after ice-out in mid May 1999, for a total of seven sampling times.

Analytical Procedures

All in-lab analyses adhered to strict quality assurance/quality control (QA/QC) protocols. A blank sample was run at the beginning of each .
which were modified from Standard Methods for the Examination of Water and Wastewater (APHA 1992).

Alkalinity, pH, and conductivity were measured within 24 hours of sampling after samples reached ambient laboratory temperature. A 50-mL aliquot of the unpreserved water sample was analysed for alkalinity and pH using the automated Mettler DL20 Compact Titrator with Mettler Probe #DG115-SC. Conductivity was measured with a VWR Digital Conductivity Meter with automated temperature compensation calibrated at 200 μS·cm⁻¹.

Total suspended solids (TSS) and total dissolved solids (TDS) were determined gravimetrically and reported as weight per volume of sample. TSS refers to all material (residue, particulate) that was removed by filtration through a 0.45-μm glass fibre filter and dried at 103°C. The TDS fraction measured the amount of dissolved material that passed through a 0.45-μm filter. This material was collected in beakers and dried at 103°C. The filters and beakers were desiccated for 12 hours, and then final weights were obtained to five decimal places. An aliquot of the unused portion of the filtered TDS sample was used to determine anion (sulfate \([\text{SO}_4]\), Cl, and nitrate \([\text{NO}_3]\)) concentrations using a Dionex DX-120 Ion Chromatograph (IC) in conjunction with an AS40 automated sampler.

Dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) were measured by converting any carbonate and bicarbonate species to carbon dioxide. DIC was measured by acidifying the sample and passing it over a carbon dioxide permeable membrane. The CO₂ gas passed through the membrane and was absorbed in a weakly buffered alkaline solution containing a phenolphthalein indicator. The decrease was detected by the Skalar SanPLUS System. DOC was measured when the sample was introduced into the Skalar where it was acidified and flushed with nitrogen gas to remove the inorganic carbon. The sample was then oxidized with an ultraviolet (UV) digester in an acid-persulfate medium. Again, the carbon was converted to CO₂, and following dialysis was measured by determining the loss in absorbance of a weakly buffered alkaline solution containing a phenolphthalein indicator.

Reactive silica (\(\text{SiO}_2\)) was analysed using the molybdate-reactive silica method. This method was based on the formation of the molybdenum heteropoly blue complex and measures only dissolved reactive silicate anions (APHA 1992). Silica in the soluble colloidal form or in the insoluble polymerized form does not react and thus was not detected by this method. Ammonium molybdate at pH 1.2 reacted with silicates to produce a yellow molybdosilicic acid complex. Since phosphates also react in this manner, oxalic acid was used. The Skalar was used to measure the absorbance of the coloured solution at 660 nm. The absorbance was proportional to the reactive silicate concentration in the original sample.

Total phosphorus (TP) and total Kjeldahl nitrogen (TKN) were digested then analyzed using a colourimetric determination on the Skalar Autoanalyser system. Before analysis, samples were treated with sulfuric acid and digested stepwise to 400°C to achieve a three-fold preconcentration. The samples were then restored to their original volume. TKN concentrations were determined spectrophotometrically at 660 nm based upon a modified Berthelot (APHA 1992) reaction. TP was simultaneously analyzed on the same sample aliquot. The digestion converted all forms of phosphorus to orthophosphate which was determined colourimetrically at 880 nm based on the ascorbic acid procedure (APHA 1992).

An aliquot of the sulfuric acid-preserved water was used for the determination of ammonia nitrogen (\(\text{NH}_4\)-N). The method was also based on the modified Berthelot reaction: ammonia was chlorinated to monochloramine which reacted with salicylate to 5-aminosalicylate. After oxidation and oxidative coupling, a green-coloured complex was formed. The absorption of the formed complex was measured spectrophotometrically at 660 nm using the Skalar.

Total metals analysis was performed after a nitric acid digest at 100°C for 12 to 24 hours resulting in a two-fold concentration of the sample. Samples were analysed using the Jarrell Ash Inductively Coupled Argon Plasma 9000 Spectrometer (ICP) for Fe, Mn, Zn, Cu, Ni, Al, B, Co, Cr, Sr, Ca, K, Mg, and Na. Only those elements that were above detection limits were included in the results.

Total hardness, expressed as calcium carbonate in milligrams per litre, is defined as the sum of the calcium and magnesium concentrations. The preferred method to compute hardness was taken from the results of separate ion determinations of calcium and magnesium in the calculation: hardness (mg·L⁻¹ of CaCO₃) = 2.497 × (Ca \([\text{mg·L}^{-1}]\)) + 4.118 × (Mg \([\text{mg·L}^{-1}]\)) (APHA 1992).

Sulphide was analyzed using a Cary SE UV-Vis-NIR Varian Spectrophotometer, based on a method outlined by the United States Environmental Protection Agency (1988).

Data Analysis

In some cases values for the chemical parameters were less than the mean detection limit (MDL), and this led to a problem with some of the statistical procedures. Such data were handled by a) removing the parameters from the analyses if the majority of the data (>90% in each parameter) were less than the MDL and b) for those parameters that had only a few values less than the MDL, the value was replaced with the MDL/2. Data analysis then proceeded in three steps:

(i) A hierarchical cluster analysis program (SPSS 2001) grouped the chemical associations in the water column in 1998 and 1999.

(ii) In order to determine the short term effects of the fish farm, repeated measures ANOVAs (analysis of variances) (SPSS 2001) determined whether the water chemistry parameters for the 1998 and 1999 data differed in concentrations between depths
(mixomolimnion, chemocline, monimolimnion) and/or years.

(iii) Longer term effects of the fish farm were assessed by comparing data from June 1992, with June 1998 and 1999, for depths of 1 m (mixolimnion), 18 m (chemocline), and 30 m (monimolimnion). The 1-m-off-of-the-bottom data was not available for 1992. Repeated measures ANOVAs were again used for this procedure.

Results

Meromictic Conditions

The results (Table 1, Fig. 2) suggested that Caland pit lake could be considered meromictic with water quality in a mixolimnion (epilimnion) that was distinctly different from a monimolimnion (hypolimnion). The chemocline started at 23 m and continued for approximately 5 m. Many of the water chemistry parameters had depth distributions typical of a meromictic lake with elevated concentrations below the chemocline. Hydrogen sulfide was less than 0.1 mg·L⁻¹. The clinograde oxygen profiles were also indicative of a meromictic environment with complete oxygen depletion below the mixolimnion (Fig. 2). With turnover, the oxygen concentrations replenished in the mixolimnion to a depth of 25 m. This is shown by the oxygen profile in the 2000 winter data (Fig. 2).

The 1998 and 1999 August temperature profiles showed thermal stratification in the mixolimnion with a defined thermocline and a hypolimnion that commenced at 15 m (Fig. 2). During the winter, ice did not form above the fish pens due to the constant fish movement, but was greater than 0.5-m thick elsewhere on the lake.

Cluster analysis of 1998 and 1999 data (Fig. 3) demonstrated this dichotomy in water quality. In both years there was a cluster of parameters that had higher levels below the chemocline (Cluster 1: conductivity, alkalinity, DIC, TDS, NO₃, SO₄, Ca, Mg, hardness, Na, Cl, K, Fe, Mn, Sr, and SiO₂) and a cluster or parameters (Cluster 2: NH₄, TP, TKN, DOC, B, pH, Temperature, DO) that were either in higher concentrations in the mixolimnion or varied little throughout the entire water column. In 1999, TP was included in the first cluster as a result of increased levels off-bottom. ANOVAs revealed that all parameters except Fe varied significantly with depth, and all parameters varied significantly with season with the exception of Fe, TKN, Na, K, TDS, and B (Table 1). The onset of winter and the corresponding turnover in the shallower regions of Caland pit lake was the main cause for variations in many of the parameters in the second cluster. DOC showed several peaks throughout the sampling season, which coincided with rainfalls.

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<th>TABLE 1. Caland pit lake water chemistry mean values*</th>
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*Units are mg·L⁻¹, except conductivity (µS·cm⁻¹) and pH.

* Significant (p < 0.05) difference between years.

* Significant (p < 0.05) difference between seasons.

* Significant (p < 0.05) difference between depth.
Aquaculture in a Meromictic Pit Lake

Water Quality Variations Between 1998 and 1999

Repeated measures ANOVAs determined which variables were significantly different ($p < 0.05$) between 1998 and 1999 (Table 1). In the monimolimnion (Cluster 1) all variables decreased in concentration from 1998 to 1999 except Fe, Sr, and Mn, which remained relatively constant. In the mixolimnion, on the other hand, NH$_4$, TP, and B increased while DOC and DO decreased. The variables which decreased in concentration in the mixolimnion and monimolimnion likely reflect dilution from increased rainfall in 1999 (889.1 mm) versus 1998 (598.4 mm), and lower temperatures (mean temperature May to October in 1999 was 13.7°C versus 14.7°C in 1998). Higher rainfall in 1999 also tended to dilute concentrations of measured parameters in the inflow drainage (Table 2). Changes in the mixolimnion, however, reflect expanded production of the fish farm, causing both NH$_4$ and TP to increase and DO to decrease.

Water Quality Changes Since 1992

Repeated measures ANOVAs determined that there were significant differences from 1992 to 1998 to 1999 for conductivity, alkalinity, Ca, TP, TKN, SO$_4$, Mg, hardness, Cl, NO$_3$, K, Na, pH, and TDS. Figure 4 shows some representative parameters. Variables that comprised Cluster 1 (Fig. 3), for example, alkalinity, conductivity, calcium and sulfate, declined in concentration in the mixolimnion and chemocline while changing little in the monimolimnion. On the other hand, the mixolimnion variables (Cluster 2), fluctuated considerably with depth from 1992 to 1999. For example, P declined from 1992 to 1998 in the chemocline and monimolimnion, and then increased in these two layers in 1999. TKN decreased significantly in concentration in the monimolimnion and chemocline from 1992 to 1998.

The most noticeable change was the depletion of oxygen in the monimolimnion. In July 1992, DO levels...
Fig. 3. Hierarchal cluster analysis using the Pearson correlation average linkage between groups for the water chemistry parameters measured in 1998 and 1999 in Caland pit lake, Ontario.
Aquaculture in a Meromictic Pit Lake

**Discussion**

**Development of Meromixis**

The results (Fig. 2) showed that Caland pit lake has become meromictic with a defined chemocline. Meromixis commonly occurs from either crenogenic causes due to the influx of saline groundwater into freshwater lakes and conversely surficial freshwater into a saline lake (Jellison and Melack 1993), or from biogenic mechanisms when there is an accumulation of solutes in the water column derived from the decomposition of organic matter (Walker and Likens 1975). In the case of Caland pit lake, surface water drainage was the main cause. Drainage from the southern and western sections of the basin generally had elevated levels of the major components of the monimolimnion (Table 2). The western drainage was the only area where the water was less than a pH of 7, and the reduced alkalinity from this drainage indicates that acid formation was occurring in this area. Apparently, the presence of limestone and dolomite (McNaughton et al. 1999) are able to buffer such acidic influxes. Drainage from the north and east was much more dilute (Table 2). This was caused either by variations in geology in this section of the basin or more channelized flow that was less impacted by contact with the exposed surface. Drainage from these areas was the source of the mixolimnion. Continued flow from these dilute drainages tended to lower the concentrations of the major cations and anions from 1992 to 1999 (Fig. 4) at all depths. The net result was a meromictic pit lake that could be characterized as a hard water, alkaline lake with a relatively high salt concentration indicated by its specific electrical conductivity and TDS values averaging 650 μS·cm⁻¹ and 470 mg·L⁻¹ in the mixolimnion to 1,090 μS·cm⁻¹ and 760 mg·L⁻¹ in the monimolimnion, respectively (Table 1). Cations were dominated by Ca/Mg and the major anion was SO₄. The concentration gradients for variables associated with the monimolimnion (Fig. 3) versus the mixolimnion have increased since 1992 (Fig. 5), indicating that the two layers are becoming more distinct for many chemical parameters.

The occurrence of SO₄ as the major anion is in contrast to the findings of Axler et al. (1992) who determined that pit lakes in northern Minnesota were dominated by HCO₃⁻. Other more saline meromictic lakes like Big Soda Lake in Nevada (Kimmel et al. 1978) and Mono Lake in California (Jellison and Melack 1993) commonly have very high concentrations of SO₄. Sulfur-reducing bacteria convert the SO₄ to H₂S which can reach concentrations of over 400 mg·L⁻¹ (Cloern et al. 1983). This is not occurring in Caland pit lake as sulfide concentrations were less than 0.1 mg·L⁻¹.

Essentially, a chemical gradient in Caland pit lake was formed that completely isolated any changes in the monimolimnion from the mixolimnion. The reverse, however, was not true. The fish farm dramatically altered the water quality throughout the water column.

**Influence of the Snow Lake Fish Farm**

Between 1998 and 1999 there was an eight-fold increase in fish production (from 20,000 kg early in 1998 to 3.

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**TABLE 2. The 1998 and 1999 inflow drainage water chemistry mean values for Caland pit lake**

<table>
<thead>
<tr>
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<td>508</td>
<td>554</td>
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*Units are mg·L⁻¹, except conductivity (μS·cm⁻¹) and pH.*

of 4 mg·L⁻¹ extended at least to a depth of 45 m, while in 1998 and 1999 DO concentrations were less than 1 mg·L⁻¹ below a depth of 23 m.
163,325 kg by the end of 1999). Associated with this increase in fish production was a compounding problem of waste production, both with food and feces. Bergheim et al. (1991) stated that only 25 to 30% of the nitrogen and phosphorus in feed is typically retained in the fish, with the remainder being lost to the environment. Undigested feed is excreted in the feces as solid waste, and the by-products of metabolism (ammonia, urea, phosphate, carbon dioxide, etc.) are excreted as dissolved wastes mostly by the gills and kidneys (Ackefors et al. 1994; Bureau and Cho 1999). Nitrogen excretion resulting from dietary protein oxidation is the major source of dissolved nitrogenous wastes. High rates of nitrogen loading as excreted ammonium may contribute to excessive algal growth, increased oxygen depletion (via nitrogenuous biochemical oxygen demand), and potentially to un-ionized ammonia (NH₃) toxicity (Axler et al. 1996). In the specific case of Snow Lake Fish Farm, we estimated that approximately one tonne per year of organic matter accumulates in the bottom of the nets, which eventually is released to the bottom strata. These effects influenced various cations, dissolved oxygen, phosphorus, and nitrogen.

Cation concentrations were lower in the mixolimnion in 1999 versus 1998. Although dilution was likely the main cause of the lowered concentrations, complexing and/or sorption on substrates such as clays, organic

**Fig. 4.** A comparison of mean values for representative water chemistry parameters collected in June 1992, 1998, and 1999 in Ca-
land pit lake, Ontario. The 1992 data were collected by MOE (unpublished data). Represented depths are: mixolimnion, chemocline, and monimolimnion.
Aquaculture in a Meromictic Pit Lake

matter, and aluminum, manganese, and iron-oxides are also known to reduce cation levels in pit lakes (Miller et al. 1996). Increased production from the fish farm operation with a corresponding increase of waste particles in the water column therefore may have further lowered the concentrations of these positively charged parameters.

The dramatic decline in oxygen levels since 1992 (in July 1992 greater than 4 mg·L⁻¹ of DO was present at 45 m, but by 1998 concentrations were less than 1 mg·L⁻¹ below a depth of 23 m [Fig. 3]) must be attributed to the fish farm activities which increased the biochemical oxygen demand of the mixolimnion. The development of similar anoxic conditions has been reported in the hypolimnion of other fish farm operations (Axler et al. 1992, 1996; Gale 1999). Between 1998 and 1999, the DO profile was further degraded as it developed a distinct negative heterograde shape in the mixolimnion (Fig. 3). During the winter, ice did not form above the fish cages. A combination of these openings and the continuous movement (literally resembling egg beaters) of the caged fish ensured dissolved oxygen replenishment in the mixolimnion to a depth of 25 m (Fig. 3). This replenishment may not have occurred if ice covered the entire pit lake.

A second mechanism that can reduce oxygen levels in meromictic lakes is the oxidation of any H₂S produced by sulphur-reducing bacteria. The highest concentrations of these bacteria are found immediately below the chemocline and above the sediment where there is an abundance of organic matter. Should overturn of the mixolimnion (or the entire water column) occur, H₂S is oxidized spontaneously by any oxygen present with a corresponding lowering of DO (Jorgensen et al. 1979). However, as mentioned previously, sulfide levels are very low in Caland pit lake and so this would not be a factor in this instance.

The expansion of Snow Lake Fish Farm rainbow trout production from 1998 to 1999 coincided with an increase in TP concentrations. TP in 1998 was generally greater than the MDL (0.005 mg·L⁻¹), but increased at all depths in 1999, especially off-bottom (average 0.02 mg·L⁻¹) and at the thermocline (Fig. 3). Comparatively, in the Minnesota Aquafarms salmonid operation of approximately 1.8 million kg, Twin City-South net pen activities caused the phosphorus to increase from 0.01 mg·L⁻¹ in 1988 to 0.094 mg·L⁻¹ in 1992, and the Sherman pit TP levels rose from <0.01 mg·L⁻¹ before aquaculture began to levels above 0.25 mg·L⁻¹ towards the end of operation in 1995 (Axler et al. 1996). Ackefors and Enell (1990) determined that 80% of the phosphorus load from net pen aquaculture is associated with solids which settle quickly to the bottom. Increased hypolimnetic anoxia associated with the decomposition of these particles could have accentuated P release from the sediment causing the observed elevated levels at the sediment-water interface in Caland pit lake in 1999.

One encouraging result was the observed recovery of ambient P concentrations once fish farming activities declined. In 1992, TP was approximately 0.01 mg·L⁻¹ which was associated with the density and feeding of chinook salmon (91,000 kg). Reduced production of fish from 1992 to 1998 caused a decline in TP to <0.005 mg·L⁻¹ by early 1998 (Fig. 4). Similarly, following the closure of Minnesota’s net pen activities, phosphorus levels decreased from 0.094 mg·L⁻¹ in 1992 to near 0.010 mg·L⁻¹ in 1994 (Axler et al. 1996).

In 1999, both TKN and NH₄ approximately doubled in concentration from 1998. This was consistent with the findings of Axler et al. (1996) who found in Minnesota that nitrogen levels (NO₃⁻ + NO₂⁻ + NH₄⁺) rose from 0.363 mg·L⁻¹ in 1988 to 2.043 mg·L⁻¹ in 1993 in response to intensive net pen aquaculture. A particular problem is NH₄ and specifically the amount of toxic free ammonia that would be present. The amount of toxic

Fig. 5. Changes in nitrate, potassium and sulfate levels in the mixolimnion and monimolimnion of Caland pit lake from 1998 to 2006. Later data are from VanCook (2003) and Goold (2008).
free ammonia increases with temperature and pH. For example, the percentage of un-ionized ammonia at a temperature of 15°C and pH of 7.5 is 0.859, whereas at pH 8.0, the percentage is 2.67 (Ackefors et al. 1994). Estimated levels of toxic free ammonia in Caland pit lake would still be well below concentrations that would be detrimental to fish, but if the observed trends continued, this could become a problem. In 1999, the NO₃-N levels decreased at each depth in Caland pit lake (Table 1), likely from denitrification caused by increasing anoxia in the monimolimnion. Similarly, Axler et al. (1995) suggested denitrification could provide some control of NO₃ build-up in Minnesota fish farms.

**Future Management of Caland Pit Lake**

The most significant result of this study was that the relatively small volume of the mixolimnion could have such a pronounced influence on the water quality of the very much greater volume comprising the monimolimnion. This has considerable implications for the management of these pit lakes.

Oxygen levels are a critical issue. It may be necessary to enhance dissolved oxygen levels in the mixolimnion through the implementation of aeration systems such as windmills, pumps, or fountains. A second strategy should be to limit input of organic material to the monimolimnion, possibly through the use of closed containment methodologies (Dodd 2000).

Continued filling of Caland pit lake could also have a devastating effect. If the input of fresh water cannot keep pace with increasing surface area, the mixolimnion volume will decrease, and the depth of the water column that is suitable for aquaculture will be severely reduced and may disappear entirely. This effect will accelerate once Caland pit lake joins with Hogarth pit lake. The sulfate level will also increase considerably after this union since Hogarth pit lake has a sulfate concentration of approximately 1,500 mg·L⁻¹, which is more than four times that of Caland pit lake (McNaughton 2001). The concentration of the outflow will therefore greatly exceed the Canadian water quality guidelines for drinking water for sulfate of 500 mg·L⁻¹ (Health Canada 2008).

Other detrimental effects may occur downstream. Effluent from tailings areas at another mine site in northwestern Ontario has been documented as causing meromictic conditions downstream leading to oxygen depletion in the monimolimnion of receiving lakes containing brook trout (Haapa-aho 2004). Another concern is downstream effects on wild rice, *Zizania palustris* L., which is a commercial crop in this area (Aiken et al. 1988). In nearby Minnesota, Section 2024 of Chapter 7050, Waters of the State, states that industrial discharges of sulfate must not exceed 10.0 mg·L⁻¹ because of the potential harm to wild rice stands (Minnesota Administrative Rules, 2010). Methods must be developed to reverse this situation. It may be feasible to reduce the sulfate concentration of drainage water and/or outflow water. One possibility is to utilize wetlands to filter the runoff from the mine (Noller et al. 1994). Another possibility is to increase the volume of the mixolimnion by inputting freshwater from nearby lakes.

As an after note, detailed water quality monitoring and research on a variety of topics (toxicity, ground water sources, wetland effects) have continued on Caland pit lake since this initial study and are contained in M.Sc. theses (Vancook 2003; Goold 2008). These studies have shown that the prediction of a reduced mixolimnion is still valid, but the timing of this occurrence has changed. Originally a filling model suggested overflow into the Seine River would occur in 2030 (Vancook 2005), but this has been revised to between 2070 and 2100 (Jackson 2007). The loss of the mixolimnion will still occur, but not until a much later date. The fish farm also decreased production and eventually closed in 2006. The result has been that the water quality in Caland pit lake seems to be improving slowly. For example, both nitrate and potassium have declined in concentration in both the monimolimnion and mixolimnion (Fig. 5). Sulfate however remains a problem and is a current focus of research to reduce its concentration. In 2009, the Government of Ontario established the Steep Rock Rehabilitation Project which is to develop, over a three year period, a management plan that will rehabilitate the two pit lakes and ensure the protection of downstream waters. Environmental hazards and site management are to be properly addressed by 2032.

**Conclusions**

In this study meromictic conditions were demonstrated in a pit lake that was formerly used for mining iron. Freshwater infl ow from surface waters was sufficient to develop a mixolimnion that in 1998 extended to a depth of 25 m. Below this was the monimolimnion that extended a further 155 m. The two layers were separated by a chemocline where cations and anions, dominated by sulfate, increased in concentration. A fish farm was established in the mixolimnion of the pit lake, and aquaculture effects in the upper layer impacted the water quality in the monimolimnion causing elevated levels of nutrients, including nitrogen, phosphorus, and potassium, and a lowering of oxygen to anaerobic concentrations. However, the effect of the mixolimnion on nutrient concentrations throughout the water column seems to be reversible. After the fish farm ceased operation, a gradual lowering of nutrients occurred in both the mixolimnion and the monimolimnion. Sulfate levels, on the other hand, have not shown the same trend of declining concentrations with time and remains a concern that needs to be remediated.
References


Received: 4 February 2009; accepted: 21 September 2009.
Spatial Variability of Reproductive and Size Characteristics of the Northern Mummichog (*Fundulus heteroclitus macrolepidotus*) Collected Near Municipal Wastewater Discharges

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Northern mummichog (*Fundulus heteroclitus macrolepidotus*) have been widely considered to be suitable for environmental effects monitoring despite concerns of spatial variability observed in energy reserves and reproductive indices. In this study, temporal and spatial variability in gonadosomatic index (GSI), liversomatic index (LSI), and condition factor (K) were examined across two sites in 2006 and 10 sites (four sites exposed to wastewater discharge; six reference sites) in 2007. In 2006 GSI, LSI, and K appeared highly variable and significantly different for both males and females. In 2007, female K and gonad weight were significantly different among all sites. For males, significant differences in K and liver weight were observed among sites. Extensive spatial variation in GSI, LSI, and K observed between reference sites suggests current standardized Canadian Environmental Effects Monitoring (EEM) methods, including effect size and duration of sampling, should not be adopted for use with the northern mummichog *F. h. macrolepidotus*.

**Key words:** gonad development, EEM, wastewater, northern mummichog, *Fundulus heteroclitus*

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**Introduction**

Industrial and municipal wastewater effluents are a major source of anthropogenic stress in coastal habitats (Nacci et al. 1999; Porter and Janz 2003; Wirgin and Waldman 2004). Wastewater effluents often contain endocrine disruptors, metabolic inhibitors, carcinogens, and other potentially hazardous agents (Swartz et al. 2003; Filby et al. 2007), which are of concern for both ecological health and human use of aquatic systems (Glasgow and Burkholder 2000; Kilgour et al. 2005). Canada has developed Environmental Effects Monitoring (EEM) regulations for pulp and paper mills (Walker et al. 2000) and metal mines (Ribey et al. 2002), and has developed a proposed bioassessment program for municipal wastewater dischargers (Kilgour et al. 2005, 2007). Currently, EEM programs are known to be effective in freshwater ecosystems (Munkittrick et al. 2002), but EEM faces challenges with marine and estuarine environments where potential sentinel species occur in highly variable habitats (Courtenay et al. 2002).

Recent studies along the Atlantic coast of North America have indicated high spatial variability in reproduction and energy reserves in resident estuarine fish species such as Atlantic silverside (*Menidia menidia*) (Conover et al. 2005; Thériault et al. 2007) and mummichog (*Fundulus heteroclitus*) (Leamon et al. 2000; Thériault et al. 2007). The northern mummichog (*Fundulus heteroclitus macrolepidotus*) is considered a suitable sentinel species and indicator of environmental health (Courtenay et al. 2002), but this suitability has been questioned due to spatial variability observed in reproductive parameters, including the gonadosomatic index (GSI), energy storage parameters such as the liversomatic index (LSI), and condition factor (K) (Leblanc et al. 1997; Couillard and Nellis 1999; Leamon et al. 2000). This variability can occur naturally or may be due to anthropogenic stressors found in the environment (Walker et al. 2000).

For fish populations, EEM monitors responses in age distribution, indicators of energy use (growth rate, fecundity), and nutritional storage (liver size, body condition) used to detect stress (Munkittrick and Dixon 1989; Adams et al. 1992; Porter and Janz 2003). One can determine population and ecological stress levels by analyzing these parameters in an appropriate sentinel species. Sentinel fish species data are compared between reference and exposed sites to determine if an effect has occurred. However, in estuarine and coastal marine environments the effect on these parameters is difficult to quantify due to fluctuating conditions such as tides, temperature, oxygen levels, and challenges with identifying reference sites in highly dynamic environments if species are highly mobile (Courtenay et al. 2002). While considerable criteria for the selection of a suitable sentinel species for freshwater habitats has been reported (Munkittrick et al. 2002), information for estuarine and marine habitats is lacking (Courtenay et al. 2002).

Recently, *Fundulus heteroclitus macrolepidotus* has been recommended as a sentinel species for wastewater
monitoring In Atlantic Canada (Courtenay et al. 2002; Galloway and Munkittrick 2006; Kilgour et al. 2007). *Fundulus heteroclitus* macrolepidotus has been used in EEM programs for pulp mills (Courtenay et al. 2002), for examining food processing effluents (Thériault et al. 2007), and for a number of coastal research programs focused on anthropogenic stress (ACAP 2006). *Fundulus heteroclitus* are small-bodied euryhaline killifish found throughout coastal environments such as estuaries, marshes, and creeks, which are often characterized by the presence of highly variable abiotic factors including temperature, dissolved oxygen, turbidity, and salinity (Blaber and Blaber 1980; Whitfield 2005; Schulte 2007). In order to survive in these dynamic environments, fishes have developed wide tolerances to these fluctuating conditions (Whitfield 1994; Stainbrook et al. 2006; Dolbeth et al. 2007). Many of these habitats have also undergone extensive anthropogenic change subjecting fishes that already live in these extreme habitats to increasing levels of stress (Stainbrook et al. 2006).

A variety of studies have used *Fundulus heteroclitus* as an environmental sentinel (Leblanc et al. 1997; Kirchhoff et al. 1999; Nacci et al. 1999; Schulte 2007; Thériault et al. 2007), and some of these studies have shown unexpected results (Leblanc et al. 1997; Kirchhoff et al. 1999; Thériault et al. 2007). Leblanc et al. (1997) reported unexplained increased reproductive effort (reproductive index) in two New Brunswick estuaries downstream of a bleached kraft pulp mill when compared with local upstream reference sites. Thériault et al. (2007) reported high variability in GSI between reference sites in northern New Brunswick, and Leamon et al. (2000) reported highly variable relationships in *F. b. macrolepidotus* between LSI, K, liver glycogen, and the RNA-DNA ratio in nearby southern Connecticut reference estuaries. Leamon et al. (2000) suggested that mummichog adapt readily to highly variable environments. Thériault et al. (2007) reported intersite variability between reference sites, suggesting a variable relationship between references. Couillard and Nellis (1999) reported similar variability in reproductive parameters observed in their study and suggested this variability may be due to reproductive timing and spawning variability. In a previous study, we examined the lunar spawning periodicity of *F. b. macrolepidotus* and identified an absence of a lunar spawning rhythm, which may contribute to the challenge of using this subspecies as a sentinel (McMullin et al. 2009).

Both Environment Canada and the U.S. Environmental Protection Agency have mandated the necessity of knowledge regarding the interaction of organisms, populations, and ecosystems with both anthropogenic and natural stressors (Environment Canada 2001; U.S. EPA 2003). It is particularly challenging to obtain this knowledge for sentinel fish species due to our lack of understanding regarding the variability associated with health-indicating parameters in natural and disturbed systems. The objective of this study was to quantify the extent of spatial variability in northern mummichog for three health-indicating parameters (GSI, LSI, and K) along the lower portions of the St. John River at similar marsh habitats upstream and downstream of known wastewater discharges. The null hypothesis states there will be no differences in the above health-indicating parameters between sites in the lower St. John River. The alternative hypothesis states that there will be differences among sites in the above health-indicating parameters in the lower St. John River.

**Materials and Methods**

Sampling began near the Reversing Falls, Saint John, New Brunswick (45.27532°N, 66.08908°W) and progressed northeast towards Kennebecasis Bay and northwest towards Grand Bay (Fig. 1). Sampling was initiated in 2006 at the Indian Town sewage outfall (E1) with comparison to a reference site at Ragged Point (R1) (Fig. 1). In 2007, the study was expanded to 10 sites, including four sewage-exposed sites (Indian Town [E1], Cedar Point [E2], Kennebecasis Park [E3], and Matthew's Cove [E4]) and six reference sites (Ragged Point [R1], Yacht Lane [R2], Renforth [R3], West Saint John [R4], Grand Bay [R5], and Oak Point [R6]) (Fig. 1). Reference sites were defined as those occurring upstream (2 to 5 km) of wastewater point source discharges with no shoreline evidence of anthropogenic waste such as human hygiene products. Exposed sites were defined as areas within a proximate distance of 50 m of known wastewater discharges. All sampling sites were located in shallow water (<2 m) at low tide within an intertidal marsh habitat as indicated by the presence of vegetation such as *Spartina* sp. and a rack line formed during early spring tides. Water samples were collected from the midwater column using polyurethane bottles. Salinity, dissolved oxygen, and temperature were then determined by placing a calibrated digital meter (YSI) probe in the bottle.

**Site Descriptions**

Site descriptions are given below for exposed (E) and reference (R) sites in the lower St. John River. Eastern Saint John County in New Brunswick includes populated areas at Millidgeville, Rothesay, Quispamsis, and Kennebecasis Park (Fig. 1). At the time of this study, the old portions of Saint John City were waiting for the installation of a municipal wastewater treatment facility.

**Exposed sites**. Site E1 was sampled in both 2006 and 2007 and was located downstream (5 m) from an untreated domestic sewage outfall in Indian Town. Substrate was anoxic at this site and extensive algal mats were present in July 2006. This site may also receive industrial effluent during high tide from a pulp and paper mill located approximately 3 km downstream at the Reversing Falls (Fig. 1). The second exposed site, E2, was located immediately downstream (1 m) of the...
Fig. 1. Map of the study sites (triangle: exposed; circle: reference) sampled along the lower portions of the St. John River, New Brunswick, Canada.

only secondary sewage treatment plant with ultraviolet (UV) filtration on the lower St. John River at Cedar Point in the Millidgeville area of the north end of the City of Saint John (Fig. 1). This area also receives waste from several raw sewage discharge lines near the Reversing Falls. In 2005, the estimated population serviced by the Cedar Point treatment plant was 15,000, and the plant’s average flow was 5,663 m³/day (unpublished data, Saint John City Wastewater Treatment Division). The facility uses an activated sludge aerated treatment with UV sterilizers. The area surrounding the second exposed site (E2) includes commercial companies, the regional hospital, a university, and business districts, which are serviced by the treatment plant or one of several raw sewage dischargers.

Site E3 was adjacent (50 m) to a residential raw sewage holding facility that captures most of the sewage discharged from the Rothesay area (Fig. 1). An intercommunity offshore interceptor sewage line joins this facility’s discharge with Renforth’s wastewater facility. The outer Kennebecasis Park holding pond has a terrain buffer which separates the pond from Kennebecasis Bay. The Kennebecasis Park wastewater facility is an aerated stabilization basin with a retention time of 27 days. This facility receives waste from Rothesay, Kennebecasis Park, and Renforth, and discharges through a deep-river pipe. The Rothesay catchment area is 1,000 hectares with an estimated population of 7,500 people (CBCL 2003). The lower end of the facility receives waste from the 104-hectare catchment area of Kennebecasis Park, a residential subdivision with an estimated population of 1,200 people, and from the 138-hectare Renforth catchment area (estimated population 1,000 people). The average daily flow for this facility in 2002 was 400 m³/day from Kennebecasis Park, and 385 m³/day from Renforth (CBCL 2003). Large algal blooms were evident
along the shore at this site. This site also contained dense shoreline vegetation including *Spartina* sp.

Site E4 was downstream (10 m) of a sewage holding pond in Quispamsis (Fig. 1). The Matthew’s Cove catchment area of 550 hectares services most of the Gondola Point area at the Matthew’s Cove wastewater treatment lagoon, and consists mostly of residential users with some small commercial use. The topography of this area is high while the lagoon itself is very low making this facility prone to high stormwater flows due to a small brook which discharges into the lagoon (CBCL 2003). During storm events this aerated stabilization lagoon’s retention time of 30 days can be reduced to 15 days, thus limiting the effectiveness of wastewater treatment. In 2002 the estimated population this lagoon serviced was approximately 4,000 people with an average flow of 1,500 m³/day (CBCL 2003). This site also experienced large algal blooms and had anoxic substrate along the shoreline.

**Reference sites.** Reference sites included sites in Milledgeville at Ragged Point (R1) and at Yacht Lane (R2). Sites were also located near Renforth (R3), West Saint John (R4), Grand Bay (R5), and at Oak Point (R6) (Fig. 1). R1, R2, R5, and R6 all had densely wooded vegetation growing to within 50 m of the shoreline. Shoreline substrate at these sites consisted mostly of fine grained sediments and soil with inshore vegetation consisting mostly of *Spartina* sp. The backshore habitat of sites R3 and R4 was residential and the substrate consisted of pebble and cobble rock. There was no aquatic vegetation at any of these sites.

**Sample Collection**

*Fundulus heteroclitus macrolepidotus* were collected using standard minnow traps (Hubert 1989) (baited with commercial dried dog food) which were deployed in shallow water (<2 m) at low tide for 24 hours and retrieved the following day at low tide. Sampling in 2006 was based on the assumption that *F. h. macrolepidotus* followed a lunar spawning pattern (McMullin et al. 2009). Samples were collected six days on either side of the full moon in June (9th to 17th), July (8th to 20th), and August (4th to 14th) at sites R1 and E1 in 2006. No fish were captured at E1 during the month of August, so August was removed from analyses. In 2007, intensive sampling at a single site was initiated to define the reproductive cycle of *F. h. macrolepidotus* (McMullin et al. 2009), using the same reference site (R1) from 2006. Timing of sampling for the present study was between June 24th and June 27th, when temporal variability in GSI decreased at peak spawning at Ragged Point (McMullin et al. 2009). At each site, two sets of five traps were joined together with rope (approximately 1 m between traps) and were deployed on the bottom at each exposed and reference sampling site. Minnow traps were located by a surface float attached to the last trap. Traps were checked daily at low tide (every 24 hours) and traps were left for three days or until approximately 40 fish were collected. However, two exposed sites (E1 and E2) yielded very small sample sizes (n < 3). No fish were captured in Grand Bay (R5). These three sites were removed from analyses, leaving four exposed and five reference sites.

Fish were transported to the laboratory, within 15 min of collection, in 20-L coolers containing ambient water which was aerated when air temperature exceeded 20°C. Fish were anaesthetized using tricaine methanesulfonate (TMS) and were examined for external parasites, tumours, and lesions. Females releasing eggs were recorded as spawning. Fish were blotted dry, and whole body weight (= 0.01 g) and total length (= 1 mm) were recorded. Gonad and liver organs were carefully removed and weighed (= 0.001 g).

**Statistical Analyses**

Variables examined included total length, whole body weight, K, GSI, and LSI during the spawning season. The gonadosomatic index was calculated as GSI = 100 × [gonad mass (g)/[total mass (g) – gonad mass (g)]]. The liversomatic index was calculated as LSI = 100 × [liver mass (g)/[total mass (g) – liver mass (g)]]. The condition factor was calculated as K = 100,000 × [total mass (g)/ [total length (mm)]³].

Power analyses was conducted to determine the power necessary to detect a 25% difference, as suggested by the national EEM program (Environment Canada 2005a), in GSI and LSI, and a 10% difference for K. Power analyses were determined using the power calculation instruction set of SAS 9.1. For better understanding of data trends, both gonad and liver weight are represented in Fig. 2 and 3 by their respective indices (gonad weight = GSI; liver weight = LSI); however, all analyses were conducted on gonad and liver weights. Comparisons of gonad and liver weight between sites were conducted separately for males and females using an analysis of covariance (ANCOVA) with body weight as the covariate and site as the independent variable. If the interaction term of the ANCOVA (body weight by site) was not significant (α > 0.05), then the interaction was removed and the analysis was rerun to identify potential effects at the site. ANCOVA was also conducted on pairs of sites for 2007 data to determine whether interactions occurred within pairs. Individual sampling days were compared between two sites for 2006 data. A one-way analysis of variance (ANOVA) was used to determine if any differences in length, body weight, and K existed among sites. Tukey studentized range tests were used as posthoc tests when the ANCOVA or ANOVA found statistical differences between sites. All data were log₁₀ transformed to meet assumptions of normality and homogeneity of the above univariate tests using the D’Agostino-Pearson normality test. Statistical analyses were performed using the POWER, ANCOVA, ANOVA, and GLM procedures of SAS version 9.1.
Results

2006 Results

During June and July 2006, a preliminary study was conducted at two sites (R1 and E1) on the lower portion of the St. John River. A total of 565 *F. h. macrolepidotus* (females: 298; males: 267) were collected. Body condition of female *F. h. macrolepidotus* varied among sampling dates in 2006, ranging from 0.82 to 1.27 with no obvious spatial or temporal patterns being evident (Table 1). In general fish tended to be smaller at the exposed site, and during July showed increased liver sizes in males and increased liver size, ovary size, and condition in females. However, the variability between dates, and the apparent absence of a lunar pattern in GSI prompted a more detailed study (McMullin et al. 2009), a tighter standardization of sampling, and an increase in the number of exposed and reference sites sampled. Females from the reference site showed higher condition on two of five occasions in June (Table 1). Females from exposed sites had a higher condition on three of the four sampling dates in July. Ovary size was significantly smaller at the exposed site on two occasions in June, and was larger at the exposed site once in June and three times in July (Table 1). Males showed similar differences between sites with body weight being lower at the exposed site for six of nine comparisons, and significantly higher only once, but there was still considerable variability among collection dates (Table 2). Males showed few differences between sites in gonad size, with differences being higher once at the exposed site, and once at the reference site (Table 2). However, liver sizes were higher twice in June, and during three of four July collections, liver sizes were as much as 125% larger at the sewage site.

2007 Regional Study

Spatial variability in three indices (K, GSI, and LSI) was examined during this short period of intensive sampling at seven sites. A total of 281 *F. h. macrolepidotus* (females: 150; males: 131) were collected (Table 3). Fish length (females: 71.07 ± 0.68 mm; males: 73.4 ± 0.74 mm) and weight (females: 4.38 ± 0.15 g; males: 5.4 ± 0.16 g) were similar to findings of our previous study (McMullin et al. 2009).

Length of female *F. h. macrolepidotus* was significantly different among sites (ANOVA, *F*(6,140) = 7.84; *p* < 0.0001) with fish from R3 being the largest and fish from E4 being the smallest. Significant difference were observed in body weight (ANOVA, *F*(6,140) = 5.19; *p* < 0.0001) and K (ANOVA, *F*(6,140) = 7.69; *p* < 0.0001) (Table 3). K varied among reference and exposed sites with 12.73% variability occurring between reference sites. Gonad weight was significantly different between sites (ANCOVA, *F*(6,139) = 8.10; *p* < 0.0001) (Fig. 2). Variability in gonad weight between reference sites was as much as 50% (Table 3). Male length (ANOVA, *F*(6,121) = 3.59; *p* = 0.0026) and weight (ANOVA, *F*(6,121) = 4.88; *p* = 0.0002) were significantly different between sites (Table 3). Significant differences were also observed in K between sites (ANOVA, *F*(6,121) = 5.52; *p* < 0.0001) and liver weight between all sites (ANCOVA, *F*(6,120) = 3.66; *p* = 0.0023) (Table 3).

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**Fig. 2.** Mean ± S.E. for GSI (%) (representing gonad weight) of female mummichog (*Fundulus heteroclitus macrolepidotus*) collected at five reference (white) and four sewage exposed (solid) sites throughout the lower St. John River in June 2007. Values for sites sharing the same alphabetical superscript are not significantly different (Tukey’s HSD, <0.05). No fish were captured at R5.

**Fig. 3.** Mean ± S.E. liversomatic index (LSI) (%) (representing liver weight) of male mummichog (*Fundulus heteroclitus macrolepidotus*) collected at five reference (white) and three sewage exposed (solid) sites throughout the lower St. John River in June 2007. Values for sites sharing an alphabetical superscript are not significantly different (Tukey’s HSD, <0.05). No fish were captured at R5.


## TABLE 1. Physiological and reproductive endpoints of female northern mummichog (*Fundulus heteroclitus macrolepidotus*)

<table>
<thead>
<tr>
<th>Site</th>
<th>Date</th>
<th>n</th>
<th>Length (mm)</th>
<th>Weight (g)</th>
<th>K</th>
<th>GSI (%)</th>
<th>LSI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>9-Jun</td>
<td>19</td>
<td>74.7±4.4</td>
<td>5.59±0.90</td>
<td>1.13±0.02</td>
<td>8.28±0.97</td>
<td>2.64±0.37</td>
</tr>
<tr>
<td></td>
<td>11-Jun</td>
<td>20</td>
<td>53.3±1.2</td>
<td>1.90±0.15</td>
<td>1.21±0.03</td>
<td>12.23±1.09</td>
<td>3.52±0.70</td>
</tr>
<tr>
<td></td>
<td>13-Jun</td>
<td>19</td>
<td>73.0±2.7</td>
<td>5.40±0.61</td>
<td>1.26±0.04</td>
<td>7.82±0.72</td>
<td>2.27±0.11</td>
</tr>
<tr>
<td></td>
<td>15-Jun</td>
<td>20</td>
<td>84.1±2.9</td>
<td>7.13±3.64</td>
<td>1.11±0.02</td>
<td>8.87±0.50</td>
<td>2.01±0.17</td>
</tr>
<tr>
<td></td>
<td>17-Jun</td>
<td>16</td>
<td>56.5±4.0</td>
<td>2.56±0.63</td>
<td>1.16±0.04</td>
<td>5.77±0.85</td>
<td>2.32±0.41</td>
</tr>
<tr>
<td></td>
<td>8-Jul</td>
<td>20</td>
<td>75.3±4.0</td>
<td>3.80±0.85</td>
<td>1.16±0.02</td>
<td>7.48±0.95</td>
<td>2.11±0.14</td>
</tr>
<tr>
<td></td>
<td>10-Jul</td>
<td>18</td>
<td>67.6±4.4</td>
<td>4.37±0.92</td>
<td>1.11±0.02</td>
<td>6.43±0.83</td>
<td>2.16±0.37</td>
</tr>
<tr>
<td></td>
<td>12-Jul</td>
<td>19</td>
<td>66.7±3.3</td>
<td>3.81±0.62</td>
<td>1.12±0.03</td>
<td>5.39±0.83</td>
<td>1.82±0.07</td>
</tr>
<tr>
<td></td>
<td>18-Jul</td>
<td>20</td>
<td>77.0±3.1</td>
<td>5.35±0.62</td>
<td>1.06±0.02</td>
<td>4.82±0.65</td>
<td>2.44±0.08</td>
</tr>
<tr>
<td>E1</td>
<td>9-Jun</td>
<td>4</td>
<td>53.3±1.4***</td>
<td>1.67±0.08***</td>
<td>1.11±0.05</td>
<td>7.32±1.49</td>
<td>4.60±1.52</td>
</tr>
<tr>
<td></td>
<td>11-Jun</td>
<td>17</td>
<td>85.9±1.6***</td>
<td>7.47±0.39***</td>
<td>1.16±0.02*</td>
<td>7.00±0.47***</td>
<td>2.48±0.16</td>
</tr>
<tr>
<td></td>
<td>13-Jun</td>
<td>12</td>
<td>46.6±0.8***</td>
<td>1.07±0.05***</td>
<td>1.06±0.04</td>
<td>7.12±0.97***</td>
<td>3.12±0.39</td>
</tr>
<tr>
<td></td>
<td>15-Jun</td>
<td>19</td>
<td>47.8±0.9***</td>
<td>1.39±0.11***</td>
<td>1.23±0.04</td>
<td>9.47±0.79</td>
<td>3.48±0.28</td>
</tr>
<tr>
<td></td>
<td>17-Jun</td>
<td>7</td>
<td>55.3±1.6***</td>
<td>1.35±0.09***</td>
<td>0.82±0.09***</td>
<td>12.33±2.28*</td>
<td>2.11±0.33</td>
</tr>
<tr>
<td></td>
<td>8-Jul</td>
<td>14</td>
<td>60.9±5.3*</td>
<td>3.24±0.82*</td>
<td>1.07±0.04</td>
<td>6.37±0.61</td>
<td>2.94±0.21*</td>
</tr>
<tr>
<td></td>
<td>10-Jul</td>
<td>13</td>
<td>48.6±1.3***</td>
<td>1.51±0.14***</td>
<td>1.27±0.04</td>
<td>9.83±1.05***</td>
<td>3.29±0.30*</td>
</tr>
<tr>
<td></td>
<td>12-Jul</td>
<td>22</td>
<td>47.1±0.7***</td>
<td>1.23±0.08***</td>
<td>1.15±0.04</td>
<td>7.92±0.79***</td>
<td>3.19±0.26***</td>
</tr>
<tr>
<td></td>
<td>18-Jul</td>
<td>19</td>
<td>48.9±1.3***</td>
<td>1.51±0.14***</td>
<td>1.25±0.03***</td>
<td>10.54±0.90***</td>
<td>2.86±0.26*</td>
</tr>
</tbody>
</table>

1 Data collected from June to July of 2006.
2 Each value represents the mean ± SE.
3 Gonad and liver size is expressed as percentage of body weight.
4 Indicates a significant difference (< 0.05) between sites.
5 Indicates a significant difference (< 0.01) between sites.
6 Indicates a significant difference (< 0.001) between sites.

## TABLE 2. Physiological and reproductive endpoints of male northern mummichog (*Fundulus heteroclitus macrolepidotus*)

<table>
<thead>
<tr>
<th>Site</th>
<th>Date</th>
<th>n</th>
<th>Length (mm)</th>
<th>Weight (g)</th>
<th>K</th>
<th>GSI (%)</th>
<th>LSI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>9-Jun</td>
<td>20</td>
<td>60.8±3.2</td>
<td>2.95±0.43</td>
<td>1.12±0.04</td>
<td>1.48±0.14</td>
<td>1.37±0.18</td>
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<tr>
<td></td>
<td>11-Jun</td>
<td>17</td>
<td>47.2±1.8</td>
<td>1.08±0.15</td>
<td>0.98±0.03</td>
<td>2.10±0.22</td>
<td>1.49±0.13</td>
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<tr>
<td></td>
<td>13-Jun</td>
<td>20</td>
<td>49.8±0.7</td>
<td>1.36±0.07</td>
<td>1.09±0.03</td>
<td>1.50±0.12</td>
<td>1.53±0.12</td>
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<tr>
<td></td>
<td>15-Jun</td>
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<td>78.2±2.9</td>
<td>5.58±0.53</td>
<td>1.08±0.04</td>
<td>0.93±0.11</td>
<td>1.13±0.09</td>
</tr>
<tr>
<td></td>
<td>17-Jun</td>
<td>16</td>
<td>69.2±3.5</td>
<td>4.00±0.58</td>
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<td>1.48±0.17</td>
<td>1.62±0.18</td>
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<tr>
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<td>48.5±1.2</td>
<td>1.17±0.10</td>
<td>0.99±0.03</td>
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<tr>
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</tr>
<tr>
<td></td>
<td>18-Jul</td>
<td>15</td>
<td>81.1±3.7</td>
<td>6.92±0.77</td>
<td>1.16±0.04</td>
<td>1.06±0.08</td>
<td>1.66±0.17</td>
</tr>
<tr>
<td>E1</td>
<td>9-Jun</td>
<td>10</td>
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<td>1.34±0.10*</td>
<td>1.04±0.05</td>
<td>3.31±1.49</td>
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<td>1.21±0.06*</td>
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<td>15-Jun</td>
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<td>55.1±4.1***</td>
<td>2.04±0.66***</td>
<td>0.91±0.03</td>
<td>1.80±0.27</td>
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<td>17-Jun</td>
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<td>43.0±1.0**</td>
<td>0.87±0.07**</td>
<td>1.09±0.05</td>
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<td>2.92±1.11**</td>
<td>2.91±0.61▲</td>
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<td>1.01±0.09</td>
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<td>2.97±0.30**</td>
</tr>
<tr>
<td></td>
<td>18-Jul</td>
<td>10</td>
<td>70.6±2.6***</td>
<td>4.31±0.48***</td>
<td>1.17±0.03</td>
<td>0.31±0.05</td>
<td>1.46±0.08</td>
</tr>
</tbody>
</table>

7 Data collected from June to July of 2006.
8 Each value represents the mean ± SE.
9 Gonad and liver size is expressed as percentage of body weight.
* Indicates a significant difference (< 0.05) between sites.
** Indicates a significant difference (< 0.01) between sites.
*** Indicates a significant difference (< 0.001) between sites.
▲ Indicates an interaction (< 0.05) between site and body weight.
Spatial Variability of Spawning Northern Mummichog

Power Analyses

Sampling times reported herein were based on low variability in GSI at the R1 reference site which was sampled intensively from May 16th to July 30th (McMullin et al. 2009). A recommended sample size of 20 individuals from each sex would achieve a power level of 99%. These data have revealed that the assumption that GSI variability was low throughout the sites sampled is true, especially for females (Table 3). Female GSI had 99.9% power at our regularly sampled reference site R1 and all reference sites had strong power (Table 4). One exposed site (E3) had weaker power at 44.5% due to a low sample size (n = 7 females) at this site. Male GSI fell below acceptable environmental monitoring limits at all sites, indicating that males require greater sample sizes than n = 20 to detect a 25% effect (Table 4).

Environmental Parameters

Temperatures collected on June 24th to 27th of 2007 on average were optimal spawning temperatures (approximately 20°C) for *F. h. macrolepidotus* and ranged from 18.5°C to 24.6°C (Table 5). Areas of the river where sites were not protected by inlets or coves (i.e., more exposed) had lower temperatures. Salinity was highest near the Reversing Falls at E1 (22.3 ppt) and lower with increasing distance from the ocean near the upstream reference sites in Kennebacasis Bay (R3, 10.2 ppt), Grand Bay (R5, 10 ppt), and Oak Point (R6, 6.1 ppt). Algal blooms were noted in areas where dissolved oxygen levels were low (E4, 5.7 mg/L).

---

**Table 3. Physiological and reproductive endpoints of northern mummichog (*Fundulus heteroclitus macrolepidotus*)**

<table>
<thead>
<tr>
<th>Sex</th>
<th>Site</th>
<th>n</th>
<th>Length (mm)</th>
<th>Weight (g)</th>
<th>K</th>
<th>GSI (%)</th>
<th>LSI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>R1</td>
<td>35</td>
<td>76.3 ± 0.6*</td>
<td>5.71 ± 0.18*</td>
<td>1.28 ± 0.02*</td>
<td>11.34 ± 0.37*</td>
<td>3.90 ± 0.14*</td>
</tr>
<tr>
<td></td>
<td>R2</td>
<td>15</td>
<td>70.0 ± 2.4*</td>
<td>4.96 ± 0.48*</td>
<td>1.41 ± 0.04*</td>
<td>16.46 ± 0.87*</td>
<td>3.92 ± 0.29*</td>
</tr>
<tr>
<td></td>
<td>R3</td>
<td>7</td>
<td>82.7 ± 6.2*</td>
<td>7.74 ± 1.52*</td>
<td>1.30 ± 0.07*</td>
<td>13.83 ± 1.23*</td>
<td>4.49 ± 0.43*</td>
</tr>
<tr>
<td></td>
<td>R4</td>
<td>27</td>
<td>71.8 ± 1.0*</td>
<td>4.72 ± 0.20*</td>
<td>1.26 ± 0.03*</td>
<td>13.02 ± 0.43*</td>
<td>4.17 ± 0.30*</td>
</tr>
<tr>
<td></td>
<td>R6</td>
<td>14</td>
<td>74.0 ± 2.5*</td>
<td>5.25 ± 0.53*</td>
<td>1.23 ± 0.03*</td>
<td>18.19 ± 0.86*</td>
<td>3.44 ± 0.38*</td>
</tr>
<tr>
<td>E1</td>
<td>2</td>
<td>85</td>
<td>8.38</td>
<td>1.34</td>
<td>16.13</td>
<td>4.85</td>
<td></td>
</tr>
<tr>
<td>E2</td>
<td>1</td>
<td>79</td>
<td>6.22</td>
<td>1.26</td>
<td>16.5</td>
<td>4.87</td>
<td></td>
</tr>
<tr>
<td>E3</td>
<td>18</td>
<td>78.5 ± 1.3*</td>
<td>6.44 ± 0.38*</td>
<td>1.31 ± 0.02*</td>
<td>11.93 ± 0.46*</td>
<td>3.77 ± 0.24*</td>
<td></td>
</tr>
<tr>
<td>E4</td>
<td>31</td>
<td>66.9 ± 1.9*</td>
<td>4.60 ± 0.36*</td>
<td>1.44 ± 0.03*</td>
<td>16.60 ± 0.83*</td>
<td>3.49 ± 0.20*</td>
<td></td>
</tr>
</tbody>
</table>

M  
| Site | R1   | 10 | 71.9 ± 2.3* | 4.43 ± 0.43* | 1.16 ± 0.02* | 1.69 ± 0.14* | 2.32 ± 0.16* |
|      | R2   | 25 | 69.2 ± 1.7* | 4.30 ± 0.39* | 1.23 ± 0.01* | 1.78 ± 0.13* | 3.62 ± 0.16* |
|      | R3   | 33 | 69.9 ± 1.1* | 3.89 ± 0.19* | 1.12 ± 0.02* | 1.81 ± 0.11* | 2.29 ± 0.14* |
|      | R4   | 13 | 70.6 ± 1.0* | 4.07 ± 0.18* | 1.15 ± 0.03* | 1.84 ± 0.21* | 1.98 ± 0.21* |
|      | R6   | 19 | 67.8 ± 1.8* | 3.69 ± 0.39* | 1.12 ± 0.03* | 1.61 ± 0.09* | 1.64 ± 0.21* |
| E1  | 3    | 72.3 ± 4.3 | 4.69 ± 0.65 | 1.23 ± 0.05 | 2.63 ± 0.10 | 1.92 ± 0.21 |
| E3  | 21   | 76.9 ± 1.9* | 5.76 ± 0.42* | 1.23 ± 0.03* | 2.15 ± 0.42* | 2.12 ± 0.31* |
| E4  | 7    | 73.7 ± 2.7* | 5.11 ± 0.63* | 1.24 ± 0.04* | 4.23 ± 2.59* | 1.79 ± 0.20* |

1 Data collected from June 2007.
2 Each value represents the mean ± SE.
3 Values for sites sharing an alphabetical superscript within each sex (F, female; M, male) are not statistically different (Tukey’s HSD, <0.05).
4 Values sharing bold site superscripts indicates an interaction (<0.05) between site and body weight.

---

**Table 4. Power levels (%) for detecting an effect on K, GSI, and LSI**

<table>
<thead>
<tr>
<th>Sex</th>
<th>Site</th>
<th>n</th>
<th>K</th>
<th>GSI</th>
<th>LSI</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>R1</td>
<td>35</td>
<td>98.9</td>
<td>99.9</td>
<td>99.7</td>
</tr>
<tr>
<td></td>
<td>R2</td>
<td>15</td>
<td>76</td>
<td>89.5</td>
<td>63.5</td>
</tr>
<tr>
<td></td>
<td>R3</td>
<td>27</td>
<td>92</td>
<td>99.9</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>R5</td>
<td>14</td>
<td>84.7</td>
<td>94.7</td>
<td>33.7</td>
</tr>
<tr>
<td></td>
<td>R6</td>
<td>18</td>
<td>99</td>
<td>99.3</td>
<td>76</td>
</tr>
<tr>
<td>E3</td>
<td>7</td>
<td>25.7</td>
<td>44.5</td>
<td>39.4</td>
<td></td>
</tr>
<tr>
<td>E4</td>
<td>31</td>
<td>95.1</td>
<td>93.7</td>
<td>84.9</td>
<td></td>
</tr>
</tbody>
</table>

M  
| R1   | 10 | 94.5 | 53.2 | 68.6 |
| R2   | 25 | 99.9 | 68.3 | 9.1 |
| R3   | 13 | 87.2 | 33.2 | 35  |
| R5   | 19 | 75.6 | 89.2 | 27.7 |
| R6   | 21 | 83.1 | 14.2 | 22  |
| E3   | 33 | 99.3 | 84.1 | 82.4 |
| E4   | 7  | 58.3 | 56.7 | 30  |

1 Data collected from June 2007.

---

**Note**: The superscript letters in the tables denote significant differences among sites. The superscript letters indicate the sites that are significantly different from each other. The superscript letters with bold indicate the sites that are significantly different from each other with a p-value less than 0.05.
TABLE 5. Environmental parameters collected

<table>
<thead>
<tr>
<th>Site</th>
<th>DO(^1) (mg/L)</th>
<th>Salinity (ppt)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>9.6</td>
<td>17.3</td>
<td>21.3 ± 3.1</td>
</tr>
<tr>
<td>R2</td>
<td>11</td>
<td>17.5</td>
<td>20.7 ± 2.4</td>
</tr>
<tr>
<td>R3</td>
<td>7.8</td>
<td>10.2</td>
<td>22.4 ± 3.6</td>
</tr>
<tr>
<td>R4</td>
<td>10.1</td>
<td>12</td>
<td>18.5 ± 3.7</td>
</tr>
<tr>
<td>R5</td>
<td>9.6</td>
<td>10</td>
<td>20.6 ± 2.8</td>
</tr>
<tr>
<td>R6</td>
<td>6.2</td>
<td>6.1</td>
<td>24.3 ± 2.3</td>
</tr>
<tr>
<td>E1</td>
<td>7.4</td>
<td>22.3</td>
<td>19.4 ± 4.3</td>
</tr>
<tr>
<td>E2</td>
<td>8.4</td>
<td>11.7</td>
<td>20.1 ± 3.9</td>
</tr>
<tr>
<td>E3</td>
<td>6.1</td>
<td>12.2</td>
<td>23.4 ± 3.5</td>
</tr>
<tr>
<td>E4</td>
<td>5.7</td>
<td>15.8</td>
<td>24.6 ± 2.6</td>
</tr>
</tbody>
</table>

\(^1\) Data collected from June 2007.
\(^2\) DO = dissolved oxygen.

Discussion

The goals of our study were to assess natural variability in health indicators (K and gonad and liver weights) in *Fundulus heteroclitus* within the lower St. John River, New Brunswick, and to determine whether this variability would affect an assessment of the potential impacts of wastewater effluents. The recommended EEM protocol was used in this assessment, which is based on pulp and paper mill and metal mine monitoring (Environment Canada 2005a). Recommended critical effect sizes for monitoring are set at 25% for gonad size and liver size, and 10% for condition (Munkittrick et al. 2002; Environment Canada 2005b).

This is not the first time variability of this extent for reproduction, energy, and condition has been observed in *F. heteroclitus*. Some authors have suggested *F. heteroclitus* is inherently variable due to the naturally variable systems in which the species are found (Couillard and Nellis 1999; Leamon et al. 2000; Thériault et al. 2007). Thériault et al. (2007) found significant differences in gonad size between regional and local (i.e., within the same harbour as the exposed site) reference sites in New Brunswick when examining the impact of a nearby food processing plant. Analyses of data from our study indicate either the local reference site was also impacted or *F. b. macrolepidotus* indices are too variable to detect a difference. Couillard and Nellis (1999) encountered similar problems during a bleached kraft pulp mill assessment in which they suggested the reason they did not obtain expected results was due to the timing of sampling around the reproductive cycle. The sampling time for this study occurred during spawning (McMullin et al. 2009) and this has made no difference in reducing spatial variability when compared with similar studies.

Analyses between sites were complicated in both years by noticeably skewed sex ratio differences occurring during spawning times at all sites. In 2007, many sites exhibited catches that were skewed in favour of one sex or the other. Spawning males, easily identified by bright yellow colourations in the field (Able and Fahay 1998), were particularly difficult to catch. High site fidelity has been reported for *F. heteroclitus*. Skinner et al. (2005) reported 617 (96.6%) mummichog returned to within 200 m of the point of initial release after one year. This small home range indicates the potential usefulness of the mummichog as a monitoring fish species. However, in this study the difficulty observed in catching either sex during the spawning phase suggests either 1) individuals from either sex leave spawning grounds after spawning or 2) all of the sites chosen in this study were not primary spawning grounds. While overall site fidelity has been reported, the extent of site fidelity during spawning is unknown and should be investigated further. This is especially important because the sampling of mummichog throughout their spawning seasons has shown that interpretation of relative gonad sizes will be strongest at the start of the spawning season, and that there is apparent site and annual variability in the pattern of gonadal changes later in the spawning season (McMullin et al. 2009).

Adaptation to anthropogenic stressors may have also complicated this study where stressors are persistent over a long period of time in the lower St. John River. Adaptation has been suggested to occur with exposure to dioxin-like compounds reported from a population in New Bedford Harbour, Massachusetts (Nacci et al. 1999). Adaptation also likely occurs in a population of *F. b. macrolepidotus* at the Sydney Tar Ponds, Nova Scotia, where high tolerance to polychlorinated biphenyl and polycyclic aromatic hydrocarbon compounds has been demonstrated (pers. comm. Dr. Martha Jones of Cape Breton University). The ability to capture bioassessment data on an indicator species exposed to sewage over many years is now diminishing in the St. John River. Potential recovery of fish populations is expected because a secondary sewage treatment facility and several primary holding facilities have been constructed. However, establishing baseline data before remedial effort will prove whether adaptation to anthropogenic stressors has occurred within the population and will help explain recovery outcomes.

In Saint John, New Brunswick, wastewater is a serious issue and the demand for monitoring wastewater dischargers and their potential interactions with ecosystem health is critical. However, the requirements for monitoring ecosystems exposed to wastewater are not well understood. Therefore, the identification of proper ecological monitoring tools such as appropriate sentinel fish species needs to be established before monitoring commences. Several local studies have attempted to use *F. b. macrolepidotus* in monitoring assessments which have revealed unsatisfactory variability in gonad size (Leblanc et al. 1997; Thériault et al. 2007). Our findings are similar to those of southern studies reporting that GSI in southern mummichog (*Fundulus heteroclitus* heteroclitus) is also variable (Leamon et al. 2000; Hunter et al. 2007). This in part relates back to the life history of the mummichog, being described as euryhaline, a...
species that is broadly tolerant to changes in salinity, and possibly temperature, given the shallow saltmarsh pans, pools, and creeks it occupies (Able and Fahay 1998).

The power of statistical tests in our study was low for detecting the EEM-suggested effect sizes of 25% for liver size and 10% for K. However, satisfactory power levels were reached with the recommended effect size of 25% for gonad size in almost all instances for both sexes during peak spawning. It is unknown whether the time of spawning for F. heteroclitus is synchronized or asynchronized among sites, however, reliable power levels should be sufficient to detect an effect.

It is highly recommended that the spatial scale of variability in GSI be established by repetitive sampling at intervals of two to three days during the entire spawning season at several adjacent and several distant nonimpacted sites that differ in habitat quality. Natural variability of spawning should be established for F. h. macrolepidotus before attempting to use this species as a sentinel. It is also recommended that wastewater monitoring studies consider increased effect sizes for gonad and liver sizes since we were unable to detect a 25% effect reliably for ecologically relevant parameters, including GSI and LSI.

Acknowledgments

The authors thank T. Barrett, K. Lippert, J. Adams, S. Melvin, T. Bosker, L. Carroll, J. Woodland, and D. Woodland for assistance in the field as well as in the laboratory. This project received financial support from the Canadian Water Network and the New Brunswick Innovation Foundation; KRM receives support from the Canada Research Chairs program.

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Received: 1 September 2009; accepted: 10 December 2009.
Influences of Human Stressors on Fish-Based Metrics for Assessing River Condition in Central Alberta

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Economic developments in Alberta have resulted in widespread changes in land use that may deteriorate river conditions for fish. Fish assemblages were characterized with index of biological integrity metrics for the heavily-developed watershed of the Battle River, Alberta. Metric relationships with human stressors were quantified using regression and information theory methods. Although the fauna comprised 14 native species, 50% of the catch was white sucker (Catostomus commersoni Lacepede, 1803). Five statistically unrelated metrics were identified as being responsive to stressors: two trophic guilds, one habitat guild, one reproductive guild, and one measure of community structure. Regression showed that the cumulative effect of human developments, indexed as road density in the basin, was negatively linked to the relative abundance of lithophils and positively linked to the relative abundance of omnivores. Agriculture also threatened the integrity of fish assemblages. Stream sections with higher cattle densities in their basins had fewer lithophils and benthic invertivores; whereas stream sections with higher nutrient concentrations contained fewer species, as well as fewer top carnivores, but more true omnivores. Understanding effects of human footprints that are expanding in western Canada will be critical to the successful management of aquatic resources.

Key words: fish assemblages, biological integrity, land-use stressors, agriculture, urban development, modelling

Introduction

The majority of landscapes in Alberta have undergone rapid changes over the last century due to growths in agriculture and petroleum-based economic activities. In the prairie-parkland region of central Alberta, as much as 98% of the landscape may have been converted to agriculture (Timoney and Lee 2001). These changes combined with recent growths in urban and suburban developments have led to cumulative land-use modifications in the majority of drainage basins (Timoney and Lee 2001). Existing, as well as proposed road networks, suburban developments, petroleum pipelines, and related infrastructure across the landscape pose serious threats to the biological integrity of aquatic ecosystems in the region. Indeed, there is widespread recognition of the extent and significance of changes in land use and cover worldwide (Allan 2004), which has led to an increase in studies that seek to develop tools for monitoring ecosystems and to establish relationships between land use and aquatic condition (e.g., Hughes et al. 1998; Daniels et al. 2002; Bramblett et al. 2005; Pont et al. 2009). Knowledge of the relationships between land use and aquatic conditions can be used to predict the extent of change in river ecosystems in response to human development and plausible alternative futures (Allan 2004; Pont et al. 2009).

Although a variety of biological indices are available for evaluating aquatic health and ecological conditions, multimetric indices such as the “index of biological integrity” (IBI) have been particularly successful as a monitoring tool (e.g., Hughes et al. 1998; Karr and Chu 1999; Lyons et al. 2001; Daniels et al. 2002; Bramblett et al. 2005; Pont et al. 2009). Multimetric indices reflect various components of biological assemblages, including taxonomic richness, habitat and trophic guild composition, and individual health and abundance. The process of selecting measurable attributes that provide reliable and relevant signals about the ecological impacts of human activities is central to making multimetric indices effective (Karr and Chu 1999). Importantly, the characteristics of biotic assemblages can change from region to region such that metrics used for assessing streams in the midwestern United States, for example, may not be applicable to the prairie-parkland region in Canada (Hughes et al. 1998; Angermeier et al. 2000). One of the obvious challenges with fish-based assessments of northern streams and rivers in western Canada is the naturally depauperate fauna. For example, Alberta includes portions of three major drainage basins (Arctic, Hudson Bay, and Mississippi River drainages), yet has only 52 native species of fishes (Nelson and Paetz 1992). The presence of fewer species reduces the number of potential candidate metrics to characterize assemblages. Further, the biota of northern rivers is thought to be dominated by habitat, trophic, and reproductive generalists adapted to unstable flow regimes with harsh, fluctuating environmental conditions (Dodds et al. 2004; Bramblett et al. 2005).
The primary objective of our study was to better understand influences of human-related stressors, operating at various spatial scales, on functional and structural attributes of the fish assemblage (i.e., metrics) for a river in central Alberta. Fish assemblage data was used to describe the biotic assemblage, a common approach in monitoring conditions of aquatic ecosystems, because fish are responsive indicators of ecological status (Karr and Chu 1999; Daniels et al. 2002; Mebane et al. 2003; Bramblett et al. 2005; Pont et al. 2009). Further, national and provincial regulations call specifically for the protection of fish and fish habitat. The selection of fish assemblage metrics was based on our catch data, published information on species habitat requirements and life history, and a review of the applicability of metrics that were successfully used in previously published IBIs (e.g., Karr and Chu 1999; Bramblett et al. 2005; Noble et al. 2007). Using regression and information theory methods, multiple hypotheses on fish assemblage responses to human stressors were examined, including effects of nutrient loading, effects of conversion of the landscape in adjacent valleys to agricultural cover, and the effects of cumulative impacts of road networks, petroleum access, and urban developments. A secondary objective was to determine which of the examined fish assemblage metrics may be useful for assessing river conditions as part of a regional IBI monitoring program in Alberta.

Methods

Study Area and Design

The study system was the Battle River in central Alberta (Fig. 1). Unusual for Alberta, this river does not originate in the Rocky Mountains, but rather has its entire watershed contained within the heavily-developed agricultural prairie-parkland ecozone of Alberta (Strong and Leggat 1992). The headwaters begin near Battle Lake (52°35′N, 114°10′W) and the river flows eastward through the prairie-parkland region for approximately 880 fluvial km to the Saskatchewan border (52°51′N, 109°59′W) (Fig. 1). The Battle River then joins the North Saskatchewan River in Saskatchewan. Typical summer flows on the Battle River are between 4 and 8 m³/s at the Alberta-Saskatchewan border. The river’s average gradient is less than 0.4 m/km. The river flows across the Edmonton-Red Deer-Calgary development corridor. This area (Census Regions 6, 8, and 11) comprised 72% of the Alberta population in the 2001 census and was one of the four densest concentrations of people in Canada (Statistics Canada 2003). Also, two water control structures occur on the river for municipal water storage and to supplement downstream flows when the river is low. The historical fish assemblage of the Battle River is comprised of 19 native fish species (Nelson and Paetz 1992).

Study sites were selected to represent the full spatial extent of the river and conditions along it (Fig. 1). However, sampling locations and the final sample size were influenced by logistical constraints and the availability of safe launches for the electrofishing boat. In the upper section of the Battle River, 40 sites were selected between Battle and Driedmeat lakes (286 fluvial km) to represent possible influences of the Edmonton-Calgary development corridor and related urban features. Downstream of this region 10 sites were selected along the length of the Battle River, from the water control structure on Driedmeat Lake to the Forestburg Reservoir (116 fluvial km). The upper subbasins of the Battle River typically support more livestock compared with lower subbasins where annually cultivated cropland is more prevalent on the landscape (Stevens and Council 2008; this study). In the lower sections, 14 sites were selected along the third reach, defined from the water control structure on the Forestburg Reservoir to the western boundary of Canadian Forces Base (CFB) Wainwright (210 fluvial km), and 20 sites from the western boundary of CFB Wainwright to the Alberta-Saskatchewan border (200 fluvial km). In general, most sites were affected by agricultural activities, although sites in the vicinity of CFB Wainwright were identified as being minimally-disturbed sites prior to field work (Fig. 1).

At each site, a 1- or 2-km sample section (nonwadeable) was identified as a discrete sampling unit. One kilometre sections were used for sampling the upper reaches of the Battle River, whereas 2-km sections were used in the lower reaches to adequately estimate species richness and relative abundance in those waters. The basin size of study sections varied considerably, ranging from 110 km² for the smallest study reach at the top of the basin to 24,780 km² for the largest study reach located near the Saskatchewan border (Table 1). River wetted width of the study sites, calculated as the average of five measurements taken along a study section, ranged from 9.3 to 57 m (Table 1).

Sampling Methods

Fish were captured by electrofishing using a throwing anode and a boat electrofisher (Coffelt VVP-15). Sampling occurred from 13 June to 13 July in 2006 and from 28 May to 21 June in 2007. Electrofishing sampling effort was recorded and was defined as seconds (s) of time the anode was “alive” with electricity while in the water (plus for short periods in the air when the anode was being thrown from the boat). Effort ranged from 1,041 to 2,579 s per 1-km site, and from 2,628 to 6,536 s per 2-km site. At each site, sampling was conducted in a downstream direction and in 500-m subsections, such that captured individuals were held for relatively short periods, and were released approximately 100 m upstream prior to sampling the remainder of the study site. All captured individuals were identified to species and were measured for weight and fork length. All
individuals were examined for deformity and disease, eroded fins, lesions, and tumors, termed “DELTs” (Daniels et al. 2002; Mebane et al. 2003).

At each electrofishing site, standardized descriptions of instream habitat (e.g., water depth, dominant substrate type) and riparian areas were made (see Stevens and Council 2008). Riparian conditions were described by integrating measurements of the percentage of cover having deep-rooted vegetation (such as tree and shrub species), the percentage of cover with multiple age classes of woody plants, including young classes, and the percentage of shorelines that were incised and
Stevens et al.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Mean</th>
<th>SD</th>
<th>Min</th>
<th>Max</th>
<th>CV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RIPARIAN VEGETATION INDEX (%)</strong>&lt;sup&gt;b&lt;/sup&gt;</td>
<td>67.1</td>
<td>21.3</td>
<td>8.3</td>
<td>93.3</td>
<td>31.7</td>
</tr>
<tr>
<td>%cover holding deep-rooted vegetation</td>
<td>72.6</td>
<td>22</td>
<td>5</td>
<td>100</td>
<td>30.3</td>
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<tr>
<td>%cover with tree establishment and regeneration</td>
<td>59.5</td>
<td>31.5</td>
<td>0</td>
<td>96</td>
<td>52.9</td>
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<tr>
<td>%unstable shoreline</td>
<td>30.7</td>
<td>22.1</td>
<td>0</td>
<td>85</td>
<td>71.9</td>
</tr>
<tr>
<td><strong>WATER QUALITY VARIABLES</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolved oxygen (DO; mg/L)</td>
<td>7.77</td>
<td>0.93</td>
<td>4.13</td>
<td>11.28</td>
<td>11.9</td>
</tr>
<tr>
<td>pH</td>
<td>8.29</td>
<td>0.14</td>
<td>7.8</td>
<td>8.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Total phosphorous (TP; mg/L)</td>
<td>0.177</td>
<td>0.09</td>
<td>0.025</td>
<td>0.382</td>
<td>51.1</td>
</tr>
<tr>
<td>Total Kjeldahl nitrogen (TKN; mg/L)</td>
<td>1.49</td>
<td>0.27</td>
<td>0.88</td>
<td>1.98</td>
<td>18.4</td>
</tr>
<tr>
<td>Ammonia-nitrogen (NH₃-N; mg/L)</td>
<td>0.053</td>
<td>0.033</td>
<td>0.008</td>
<td>0.118</td>
<td>61.1</td>
</tr>
<tr>
<td>Nitrite+nitrate nitrogen (NO₂⁻+NO₃⁻; mg/L)</td>
<td>0.111</td>
<td>0.217</td>
<td>0.003</td>
<td>0.792</td>
<td>194.3</td>
</tr>
<tr>
<td><strong>LANDSCAPE VARIABLES</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cattle density per ha in basin</td>
<td>0.453</td>
<td>0.104</td>
<td>0.317</td>
<td>0.655</td>
<td>23</td>
</tr>
<tr>
<td>Manure application rate in basin (t per ha)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.34</td>
<td>1.17</td>
<td>2.78</td>
<td>6.65</td>
<td>27.1</td>
</tr>
<tr>
<td>%adjacent agricultural cover, 10-km upriver</td>
<td>28.3</td>
<td>13.1</td>
<td>6.2</td>
<td>52.4</td>
<td>46.5</td>
</tr>
<tr>
<td>%agricultural cover in basin</td>
<td>26.2</td>
<td>15.4</td>
<td>0.5</td>
<td>44.7</td>
<td>58.6</td>
</tr>
<tr>
<td>%adjacent cropland cover, 10-km upriver</td>
<td>19.5</td>
<td>11.5</td>
<td>2.3</td>
<td>46.5</td>
<td>59</td>
</tr>
<tr>
<td>%cropland cover in basin</td>
<td>21</td>
<td>13</td>
<td>0</td>
<td>35.4</td>
<td>61.9</td>
</tr>
<tr>
<td>%urban cover in basin</td>
<td>0.7</td>
<td>0.7</td>
<td>0</td>
<td>2.2</td>
<td>98.8</td>
</tr>
<tr>
<td>Road density in basin (m/ha)</td>
<td>12.4</td>
<td>1</td>
<td>10.6</td>
<td>14.2</td>
<td>8.3</td>
</tr>
<tr>
<td>Basin size (ha)</td>
<td>775,165</td>
<td>734,536</td>
<td>11,096</td>
<td>2,478,024</td>
<td>94.8</td>
</tr>
<tr>
<td>Mean wetted width (m)</td>
<td>19.9</td>
<td>7.4</td>
<td>9.3</td>
<td>37</td>
<td>37.3</td>
</tr>
<tr>
<td>Mean maximum depth (m)</td>
<td>1.9</td>
<td>0.6</td>
<td>1</td>
<td>4</td>
<td>29.8</td>
</tr>
</tbody>
</table>

<sup>a</sup> SD = standard deviation; CV = coefficient of variation.

<sup>b</sup> Integrates measurements of riparian vegetation (i.e., calculated as the average of %cover deep-rooted vegetation, %cover with tree establishment and regeneration, and %unstable shoreline).

<sup>c</sup> Derived from cattle density estimates by Knaga and Makowec (2008).

TABLE 1. Summary statistics of focal variables used for describing Battle River sections sampled for fish during 2006 and 2007 (n = 80)

showing signs of instability (Table 1). Water quality samples were collected during mid- to late-June 2007, after electrofishing, at the start point for each sampling site. Samples were submitted to a CAEAL (Canadian Association for Environmental Analytical Laboratories) accredited laboratory within 24 hrs of collection for analysis. Laboratory tests included those for dissolved nitrite plus nitrate as nitrogen (NO₂⁻+NO₃⁻; mg/L), total Kjeldahl nitrogen (TKN; mg/L), pH, total phosphorous (TP; mg/L), and total ammonia as nitrogen (NH₃-N; mg/L). Field meters were also used to record dissolved oxygen (DO) (mg/L), pH, and conductivity (μS/cm) at the approximate time and location of the sampling.

Using ArcGIS 9.2 and a provincial digital elevation model (DEM; 1:20,000), study watersheds were delineated and basin sizes were calculated at each study site. The adjacent landscapes were also characterized at the spatial scale of 10-km upriver by 5-km wide, perpendicular from the stream bank. The upriver starting point for a study site was the drainage point for basin and subbasin delineations. Next, multiple GIS (geographic information system) layers were obtained to create variables describing human land-use activities and stressors. These layers included the provincial cropland and hay pasture insurance database from Alberta Agriculture Financial Services (based on 2007 information), and a livestock (cattle and calves) database from Alberta Agriculture, Food, and Rural Development (based on 2001 census). The majority of agricultural cover in the study basin was in cropland (Table 1). Spatial data on human settlements were obtained from Alberta Sustainable Resource Development (ASRD; based on 2001 coverage), specifically urban cover for municipalities with a population greater than 1,000, with a majority of the buildings on parcels of land less than 1,850 m². As a correlate of cumulative effects of urban-related stressors and petroleum infrastructure, spatial data on Alberta road networks of gravel and paved access routes were also obtained, including routes to and from approximately 15,000 oil and gas well sites in the watershed. Using these layers, upriver land-use activities were quantified at two spatial scales per study site: basin-wide measurements for all land-use stressors, plus smaller-scale (i.e., subbasin) measurements of agricultural cover, 10 km upriver from the study site by 5 km, perpendicular to the stream bank (Table 1). Biological responses can be expected to change with varying spatial scales in which the stressor may operate (Allan 2004). Further, land use in riparian areas may not mirror land-use trends throughout the drainage basin. Urban cover, in general, was not in close proximity.
to the study river (C. E. Stevens, unpublished data), and therefore urban cover was assessed at the basin-level only. Also, the assessments of cattle densities were limited to the basin-level because of the coarse-scale at which these measurements were obtained.

**Metric Evaluation**

The composition of the fish catch, as well as the life history requirements of the study species were considered in the selection of candidate IBI metrics (Nelson and Paetz 1992; Simon 1999; Bramblett et al. 2005). Candidate metrics reflected various functional guilds and structural components of ecosystems and were similar to those successfully used in other IBIs (Karr and Chu 1999; Bramblett et al. 2005; Noble et al. 2007). Further, candidate metrics included those adopted in systems that were geographically near to Alberta and the Battle River; for example, proportion of lithophils and long-lived individuals were used in streams in Montana (Bramblett et al. 2005). “Tolerance to disturbance” metrics were based on rankings (1 to 10) of study species in Whittier et al. (2007). For the Battle River, study species with ranks >8 were identified as being tolerant species (i.e., fathead minnow [*Pimephales promelas* Rafinesque, 1820]), mooneye [*Hiodon tergisus* Lesueur, 1818], and goldeye [*Hiodon alosoides* Rafinesque, 1819]), and species with ranks <6 were identified as being intolerant species (i.e., longnose sucker [*Catostomus catostomus* Forster, 1773], lake chub [*Couesius plumbeus* Agassiz, 1850], and burbot [*Lota lota* Linnaeus, 1758]). For tolerance and guild-based metrics, units (i.e., percent relative abundance, number of species) were selected upon consideration of the catch data and inherent limitations of our dataset. In total, 12 candidate metrics were hypothesized as being either positive- or negative-scoring IBI metrics (Table 2). Positive-scoring metrics were those that increase in value as biological integrity increases, whereas negative-scoring metrics were those that decrease in value as biological integrity decreases (Karr and Chu 1999).

Statistical analyses began with identifying metrics that were statistically redundant (Hughes et al. 1998; Lyons et al. 2001). In other words, with a future multimetric index in mind, recommended metrics were those that were only weakly correlated with each other (Pearson $r < 0.8$). Next, candidate metrics were screened for responsiveness to human stressors using multivariate regression and an information-theoretic approach that ranked a priori models (Burnham and Anderson 2002). Importantly, if a pair of covariates had an $r > 0.8$, one of the two covariates were considered for removal from the proposed model to minimize multicollinearity. Of the water quality variables, NH$_3$-N was positively correlated with TP, and therefore was removed from models (Pearson $r = 0.83$). It is important to note that basin size was negatively correlated with cattle density in the basin (Pearson $r = -0.82$), but positively correlated with percent agricultural cover in the basin (Pearson $r = 0.91$). Thus, for each candidate metric, six a priori hypotheses or models were developed considering the stressor covariates and their relationships with one another. To minimize multicollinearity, agricultural and global models included either basin area or variables measuring agricultural stressors in basins. All models with the exception of one agricultural model (Model 3) and one global model (Model 6) comprised basin area as a proxy of both stream size and position (see below). Stream size can be an important factor structuring fish assemblages (e.g., Karr and Chu 1999; Fischer and Paukert 2008), whereas stream position can be an important determinant of fish assemblages on systems fragmented by dams (Hitt and Angermeier 2008). The following six models were tested:

**Model 1.** Water quality model = Basin area, NO$_2$+NO$_3$-N, TKN, TP, and DO.

**Model 2.** Agricultural model I = Basin area, percent adjacent agricultural cover, and riparian vegetation index.

**Model 3.** Agricultural model II = Livestock density in basin, percent agricultural cover in basin, percent adjacent agricultural cover, and riparian vegetation index.

**Model 4.** Road model = Basin area and road density in basin.

**Model 5.** Global model I = Basin area, NO$_2$+NO$_3$-N, TKN, TP, DO, percent adjacent agricultural cover (10-km upriver), riparian vegetation index, and road density in basin.

**Model 6.** Global model II = NO$_2$+NO$_3$-N, TKN, TP, DO, livestock density in basin, percent agricultural cover in basin, percent adjacent agricultural cover, riparian vegetation index, and road density in basin.

Postestimation procedures for all regressions included the Cook-Weisberg heteroscedasticity test. If errors were heteroscedastic, robust regression was used, which is an iterative procedure that reweights the observations so that highly influential ones are down-weighted (Davidson and MacKinnon 1985; Hoffman 2004). Also, variance inflation factors (VIFs) were reviewed as a postestimation procedure for ensuring that multicollinearity problems were avoided (Hoffman 2004). These tests resulted in percent urban cover being removed from the road model and subsequent analyses. Importantly, this does not imply that urban cover is unimportant as a stressor, but rather that road density may be an adequate descriptor of urban cover (Pearson $r = 0.75$ for percent urban cover and road density in subbasins of the Battle River).

Akaikes information criterion, corrected for small sample sizes (AIC$_c$), was used as a basis to select models (Burnham and Anderson 2002). Primary inferences were drawn from the best model (AIC$_{min}$) and others within
Stevens et al.

However, if the top model had a low $R^2$ value (<0.2), we concluded that the metric may be “insensitive” to human stressors and that further research may be required to confirm metric-stressor relationships. Akaike weights ($w_i$) were also calculated to assess evidence supporting each model, and to estimate model-averaged coefficients. Model averaging is a robust method that reduces model selection bias (Burnham and Anderson 2002). A metric was recommended for IBI development if model averaging confirmed anticipated responses to measures of anthropogenic disturbance, and if the direction of relationships were relatively consistent. For example, a recommended metric could be one that was identified a priori as being a positive-scoring metric (i.e., as having values that increase with biological integrity) and was negatively correlated with TP concentrations, but was positively correlated with the riparian vegetation index. A metric was not recommended for evaluating river condition if the number of predicted relationships was equal to or lesser than the number of nonexpected relationships.

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**TABLE 2.** Fish assemblage (IBI) metrics examined, including means and ranges from 2006 and 2007 fish catch data collected on the Battle River, Alberta ($n = 80$).a,b

<table>
<thead>
<tr>
<th>Candidate Metric</th>
<th>Description</th>
<th>Mean (range)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>POSITIVE-SCORING</strong></td>
<td><strong>VALUES INCREASE WITH INCREASING BIOLOGICAL INTEGRITY</strong></td>
<td></td>
</tr>
<tr>
<td>Species richness</td>
<td>A decline in taxa richness is generally one of the most reliable indicators of degradation or disturbance</td>
<td>4.2 (0–8)</td>
</tr>
<tr>
<td>Percent lithophils (TRPR, SHR)</td>
<td>Relative abundance expected to decline with higher sedimentation, reducing availability of gravel substrate for spawning</td>
<td>5.9 (0–28%)</td>
</tr>
<tr>
<td>Percent top carnivore ( Apex predator: wall, NRPK, BURB)</td>
<td>I high relative abundance of top carnivores indicates a relatively healthy, productive, and diverse community</td>
<td>21 (0–100%)</td>
</tr>
<tr>
<td>Number of benthic invertivorous species (LNSC, SHR, SHRD, IWDW, TRPR)</td>
<td>Number species expected to decline when river habitats become excessively silty and eutrophic and dissolved oxygen is reduced</td>
<td>1.1 (0–4)</td>
</tr>
<tr>
<td>Percent of benthic invertivorous individuals (LNSC, SHR, SHRD, IWDW, TRPR)</td>
<td>As above</td>
<td>16 (0–82%)</td>
</tr>
<tr>
<td>Percent older, long-lived fishes a (NRPK &gt;600 mm, WALL &gt;450 mm, WHSC &gt;400 mm, GOLD &gt;350 mm)</td>
<td>Older fish indicative of stable habitat, reduction in anthropogenic disturbance, and river connectivity</td>
<td>7.3 (0–60%)</td>
</tr>
<tr>
<td>Percent invertivorous cyprinids (LKCH, LNDC, SPSH)</td>
<td>Relative abundance expected to decline when invertebrates decrease in abundance and diversity due to habitat degradation</td>
<td>16 (0–80%)</td>
</tr>
<tr>
<td>Percent intolerant (LNDC, LKCH, BURB)</td>
<td>Includes individuals of species that have tolerance to disturbance values &lt; 6; expected to decrease as river conditions are degraded</td>
<td>6.1 (0–72%)</td>
</tr>
<tr>
<td>Total individuals in sample (catch per 100 s)</td>
<td>Total abundance is comparable to the overall ability of the river to support a community; sites in poor condition are expected to support few individuals</td>
<td>1.5 (0–4)</td>
</tr>
<tr>
<td><strong>NEGATIVE-SCORING</strong></td>
<td><strong>VALUES DECREASE WITH INCREASING BIOLOGICAL INTEGRITY</strong></td>
<td></td>
</tr>
<tr>
<td>Percent true omnivore (WHSC, FTMN)</td>
<td>As habitat declines in quality, the proportion of individuals that are omnivores is expected to increase</td>
<td>55 (0–100%)</td>
</tr>
<tr>
<td>Percent tolerant (MOON, GOLD, FTMN)</td>
<td>Individuals of species that have tolerance to disturbance values &gt; 8; expected to increase in abundance as river conditions are degraded.</td>
<td>4.8 (0–55%)</td>
</tr>
<tr>
<td>Percent Delt (deformities, disease, parasites, fin erosion, lesions or tumours)</td>
<td>These body conditions occur frequently where harmful chemicals are concentrated and can reflect stress caused by highly polluted waters.</td>
<td>25 (0–100%)</td>
</tr>
</tbody>
</table>

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a Sources: Karr and Chu (1999); Bramblett et al. (2005); Stevens and Council (2008); Noble et al. (2007); Whittier et al. (2007).

b Abbreviations: LNDC = Longnose Sucker; SHR = Shorthead Redhorse; WHSC = White Sucker; FTMN = Fathead Minnow; LKCH = Lake Chub; LNDC = Longnose Dace; SP = Spottail Shiner; NRPK = Northern Pike; BURB = Burbot; GOLD = Guldye; MOON = Mooneye; IWDW = Iowa Darter; WALL = Walleye; TRPK = Trout-perch.

c Length classification based on unpublished, provincial data collected by M. Sullivan.
Results

Of the 19 species known to occur in the Battle River, only 14 species were captured on the 80 sections sampled for fish. Catch-per-unit-effort was 0.88 fish per minute of electrofishing. In total, 3,473 fish were captured, of which the most abundant species was white sucker (49% of catch; Catostomus commersonii Lacepede, 1803). The remainder of the catch was comprised of 15.8% longnose dace (Rhinichthys cataractae Valenciennes, 1842), 11.5% lake chub, 9.8% northern pike (Esox lucius Linnaeus, 1758), 6.6% shorthead redhorse (Moxostoma macrolepidotum Lesueur, 1817), 3.3% trout-perch (Percopsis omiscomaycus Walbaum, 1792), 2.4% walleye (Sander vitreus Mitchell, 1818), 0.9% fathead minnow, 0.3% burbot, 0.2% spottail shiner (Notropis budsonius Clinton, 1824), 0.2% goldeye, 0.1% mooneye, 0.06% Iowa darter (Etheostoma exile Girard, 1859), and 0.03% longnose sucker. The latter four species were also relatively rare occurring on less than 5% of the study sites. The five species known to occur in the Battle River, but not captured during our study included the quillback sucker (Carpoides cyprinus Lesueur, 1817), emerald shiner (Notropis atherinoides Rafinesque, 1818), brook stickleback (Culaea inconstans Kirtland, 1840), yellow perch (Perca flavescens Mitchell, 1814), and lake whitefish (Coregonus clupeaformis Mitchill, 1818).

The fish catch data were used to create 12 candidate metrics, some of which were redundant as determined by correlation analysis (Pearson $r > 0.8$). For example, the “percent invertivorous cyprinids” metric was positively correlated with the “percent benthic invertivorous individuals” metric. Also, the “number of benthic invertivorous species” metric was positively correlated with the “native species richness” metric.

Insufficient variation was explained for 5 of the 12 metrics using the suite of parameters and models that were constructed. In other words, for five metrics, the $R^2$ value was less than 0.2 for the respective top model identified by AICc. These metrics were: percent older, long-lived individuals; catch per 100 s of electrofishing; percent DELTs; percent tolerant; and percent intolerants (Table 3). For the remaining seven metrics, approximately 39 to 57% of the variation in values was explained. Confidence intervals (95%) of model-averaged coefficients indicated that all seven metrics, with the exception of percent true omnivores, were influenced by basin area (Table 4). Five metrics behaved as expected and were clearly linked to human stressors, based on the 95% confidence intervals (Table 2 and 4). Metrics that were useful for evaluating river condition included: species richness, which was negatively linked to TP concentrations; percent top carnivores, which was negatively related with TKN; percent true omnivores, which was positively related to TP and road density in the basin (Fig. 2); percent benthic invertivorous individuals, which was negatively related to TP and cattle density in the basin; and percent lithophils, which was negatively linked to TP, cattle density in the basin, and road density in the basin (Table 4). Two metrics responded unexpectedly to human stressors. High numbers of benthic invertivorous species occurred in river sections with high concentrations of TKN and high levels of agricultural cover in the basins. Also, the relative abundance of invertivorous cyprinids was higher in river sections with elevated concentrations of TKN and nitrate-nitrite-N (Table 1 and 4).

Plausible stressor models, as determined by AICc, for the five metrics highlighted above were typically the water quality model (Model 1) and the road model (Model 4; also see Table 3). The water quality model was selected for predicting species richness, percent benthic invertivorous individuals, percent top carnivores, and percent lithophils; whereas the road model was selected for predicting species richness, percent true omnivores, and percent lithophils. The agricultural models (Models 2 and 3) were chosen for modelling changes in species richness (Table 3).

Discussion

This study demonstrated strong linkages between fish assemblage attributes and human stressors related to urban and agricultural activities that may impair river conditions. Relatively wide gradients of disturbance were identified along the Battle River (see variability of parameters in Table 1) where simple, northern fish assemblage attributes responded as strong indicators to the effects of human activities. Despite the inherent challenges of an assemblage dominated by white sucker, the most abundant species, five metrics were identified as being sensitive to nutrient concentrations, likely from runoff from agriculture related to cattle manure, and from urban-related influences statistically indexed as road density in basins. Importantly, the five fish assemblage metrics were statistically unrelated and conceptually different and may prove useful if integrated as a biological index for assessing river conditions.
### TABLE 3. Model rankings (according to Akaike's information criterion corrected for small sample sizes; AICc), as well as fit of models ($R^2$), predicting metric scores for the Battle River.\(^{a,b}\)

<table>
<thead>
<tr>
<th>Metric</th>
<th>Model</th>
<th>$n$</th>
<th>$df$</th>
<th>LL</th>
<th>AICc</th>
<th>$\Delta$AICc</th>
<th>Weight</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Species richness</strong></td>
<td>Water quality</td>
<td>80</td>
<td>6</td>
<td>-143.89</td>
<td>309.0</td>
<td>1.8</td>
<td>0.13</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>Agriculture I</td>
<td>80</td>
<td>4</td>
<td>-145.28</td>
<td>299.1</td>
<td>0.0</td>
<td>0.34</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>Agriculture II</td>
<td>80</td>
<td>5</td>
<td>-144.31</td>
<td>294.4</td>
<td>0.3</td>
<td>0.28</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>Road</td>
<td>80</td>
<td>3</td>
<td>-146.92</td>
<td>302.2</td>
<td>1.1</td>
<td>0.20</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>Global model I</td>
<td>80</td>
<td>9</td>
<td>-141.67</td>
<td>303.9</td>
<td>4.8</td>
<td>0.03</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>Global model II</td>
<td>80</td>
<td>10</td>
<td>-140.86</td>
<td>304.9</td>
<td>5.8</td>
<td>0.02</td>
<td>0.54</td>
</tr>
<tr>
<td><strong>No. of benthic invert. spp.</strong></td>
<td>Water quality</td>
<td>80</td>
<td>6</td>
<td>-92.58</td>
<td>198.3</td>
<td>6.2</td>
<td>0.04</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>Agriculture I</td>
<td>80</td>
<td>4</td>
<td>-101.77</td>
<td>212.1</td>
<td>20.0</td>
<td>0.00</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>Agriculture II</td>
<td>80</td>
<td>5</td>
<td>-96.14</td>
<td>203.1</td>
<td>11.0</td>
<td>0.00</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>Road</td>
<td>80</td>
<td>3</td>
<td>-101.90</td>
<td>210.1</td>
<td>18.0</td>
<td>0.00</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>Global model I</td>
<td>80</td>
<td>9</td>
<td>-90.17</td>
<td>200.9</td>
<td>8.8</td>
<td>0.01</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>Global model II</td>
<td>80</td>
<td>10</td>
<td>-84.47</td>
<td>192.1</td>
<td>0.0</td>
<td>0.94</td>
<td>0.68</td>
</tr>
<tr>
<td><strong>% benthic invertivores</strong></td>
<td>Water quality</td>
<td>80</td>
<td>6</td>
<td>42.42</td>
<td>-71.7</td>
<td>0.0</td>
<td>0.68</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>Agriculture I</td>
<td>80</td>
<td>4</td>
<td>36.58</td>
<td>-64.6</td>
<td>7.1</td>
<td>0.02</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>Agriculture II</td>
<td>80</td>
<td>5</td>
<td>32.75</td>
<td>-54.7</td>
<td>17.0</td>
<td>0.00</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>Road</td>
<td>80</td>
<td>3</td>
<td>36.74</td>
<td>-67.2</td>
<td>4.5</td>
<td>0.07</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>Global model I</td>
<td>80</td>
<td>9</td>
<td>44.93</td>
<td>-69.3</td>
<td>2.4</td>
<td>0.20</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>Global model II</td>
<td>80</td>
<td>10</td>
<td>44.02</td>
<td>-64.9</td>
<td>6.8</td>
<td>0.02</td>
<td>0.58</td>
</tr>
<tr>
<td><strong>% invertivorous cyprinids</strong></td>
<td>Water quality</td>
<td>80</td>
<td>6</td>
<td>29.75</td>
<td>-46.4</td>
<td>0.0</td>
<td>0.82</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>Agriculture I</td>
<td>80</td>
<td>4</td>
<td>23.70</td>
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<tr>
<td><strong>% older, long-lived</strong></td>
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*TABLE 3 continued on next page*
conditions in central Alberta. The five fish assemblage metrics represented two trophic guilds (i.e., percent top carnivores and true omnivores), one habitat/trophic guild (i.e., percent benthic invertivorous individuals), one reproductive guild (i.e., percent lithophils), and one measure of community structure (i.e., species richness). The abundances of omnivores and lithophils in the Battle River fish catches were highly sensitive to changes in road density in basins. Road density may affect fish assemblages through a variety of mechanisms, such as pollution, hydrologic alteration, stream channelization, fragmentation from improperly maintained culverts, and elimination of nursery habitat (Allan 2004; Wheeler et al. 2005). Road density is clearly a surrogate for a variety of anthropogenic effects and thereby is a simple measure of the cumulative human footprint. The relationship of road networks with urban development is intuitive, and as road networks and urban development grows, changes in river habitat, water chemistry, and in the integrity of fish assemblages are anticipated. Similar to the presence of networks of roads, urban development continually affects streams and causes extensive and chronic impacts to natural hydrology and chemistry (Grapentine et al. 2004), often at greater magnitudes than other land-use types (reviewed in Wheeler et al. 2005). Previous research has shown that even low levels of urban land cover in a basin (8 to 10%) can result in highly altered fish communities (Wheeler et al. 2005). The highest level of urban cover in our study basins was much lower than this threshold (ca. 2%), approaching low intensity development. However, urban cover levels in the Battle River basin may be higher if considering both urban and suburban (e.g., acreage and intensive rural subdivision) developments. Importantly, our measurements of road network densities may suffice to encompass all residential development aspects, as well as industry, such as the petrochemical sector.

The current study provided evidence that current agricultural practices may also threaten the integrity of fish assemblages. A possible mechanism for the observed effects (i.e., reductions in benthic invertivores and lithophils) may be increased sediment and nutrient runoff, causing changes in the composition of basal algal resources and a reduction in available spawning substrates (Berkman and Rabeni 1987; Carpenter et al. 1998; Little et al. 2003). A major nonpoint source of nutrients in agricultural landscapes is often manure from livestock (Carpenter et al. 1998). Although the relationship between fish assemblage metrics and cattle densities may be partially confounded by influences of stream size, we identified that both TP and TKN were important variables related to fish assemblage metrics. This trend was noted despite sampling water and fishes at different times and the associated seasonal variability that may have been introduced by this approach. Previously, researchers have suggested that the effects of

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<th>( df )</th>
<th>( LL )</th>
<th>( AIC_c )</th>
<th>( \Delta AIC_c )</th>
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<th>( R^2 )</th>
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<tr>
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<tr>
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a Highlighted rows are top models (i.e., models with AIC\(_{min}\)).
b\( df \) = degrees of freedom; \( LL \) = Log-likelihood.
agricultural practices on aquatic ecosystems in Alberta are a serious concern (Little et al. 2003; Wuite et al. 2007). For example, water contamination and nutrient loading have been observed in the Little Bow River, where repeated annual and seasonal applications of manure to the landscape may have led to high accumulation of nutrients in the soil, thereby creating a potential for pollution of surface water and groundwater (Little et al. 2003). To minimize contamination of water resources, the Agricultural Operation Practices Act (Alberta Agriculture, Food and Rural Development 2001) has laid out standards pertaining to the containment and application of manure. For example, specific setback distances are required (e.g., 30-m buffers from mechanical spreading of manure), and operators, such as those for confined feeding operations, must demonstrate that there is access to enough land to accommodate manure from their livestock. Given the results from our study and the fact that Alberta has the highest percentage of cattle in the country (Statistics Canada 2006), it is recommended

Stevens et al.

<table>
<thead>
<tr>
<th>TABLE 4. Regression summary of model-averaged coefficients (and 95% confidence intervals) for predicting fish assemblage metric scores for the Battle River*</th>
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<tr>
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<tr>
<td>TP (mg/L)</td>
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<tr>
<td>TNK (mg/L)</td>
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<tr>
<td>Nitrate+nitrite-N (mg/L)</td>
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<tr>
<td>Cattle in basin (per ha)</td>
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<tr>
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<tr>
<td>Agriculture nearby (&lt;10km, %)</td>
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<tr>
<td>Riparian condition at site (%)</td>
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<td>Road density in basin (m/ha)</td>
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<td>Agriculture nearby (&lt;10km, %)</td>
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<td>Road density in basin (m/ha)</td>
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*Intervals that do not contain zero are highlighted.
†Coefficients multiplied by 1,000,000.

44
that current practices be evaluated through biological monitoring as part of an adaptive management strategy for ensuring the conservation of aquatic resources into the future.

This study builds on the bioassessment literature from the United States, and sets a precedent for biological monitoring in western Canada. Although the conclusion of the utility of using fish assemblages as indicators of human activities was similar to Bramblett et al. (2005) in Montana, the details of our study differed from that observed for Great Plains streams. First, the use of fish condition and tolerance guilds, as defined in our study, was not supported. Second, the use of the relative abundance of true omnivores and top carnivores as trophic guild metrics was supported in this study; as opposed to metrics measuring relative abundance of invertivorous cyprinids and number of benthic invertivorous species (see Bramblett et al. 2005). Although discrepancies among studies may be an artifact of different study designs and statistics, outcomes may also vary if the composition of fish assemblages changes from one region to the next. For example, only 14 species were captured in this Battle River study, compared with 37 species described in Bramblett et al. (2005). Further, white sucker was the dominant species in the Battle River fish catch and appeared to be very tolerant to human stressors. Thus, it is not surprising that the percent older, long-lived metric could not be linked to disturbance when white sucker was included in this metric. Further, Noble et al. (2007) contend that long-lived species may have great plasticity and may adapt their life histories to survive under different conditions. Discrepancies among studies may also occur if study regions differ in environmental conditions and individual species differ in their tolerance to disturbance. It is recommended that future research identify species tolerance ranges, as well as nonlinear responses to human disturbances in northern systems, for the advancement of multimetric monitoring indices in western Canada.

In summary, by linking metric scores to descriptions of human activities made in a GIS environment, managers can easily forecast conditions under various landscape scenarios of human development (for example, see Fig. 2). Importantly, the five metrics highlighted in this study could be integrated and used as a rapid assessment tool to characterize aquatic ecosystem health. Determining whether the stressor relationships identified in this study can be extrapolated to other systems outside of the Battle River watershed will require additional sampling in new subbasins and verification of relationships. However, the Battle River is a centrally-located river comprised of species that are distributed throughout most of the province and neighboring Saskatchewan, including the North Saskatchewan River drainage basin to the north and the Red Deer River drainage basin to the south (Nelson and Paetz 1992). Further, the land uses and stressors documented in the Battle River drainage basin are present in and as much a threat to river conditions in other areas of Alberta (Cooke and Prepas 1998; Timoney and Lee 2001; Little et al. 2003). Thus, the stressor relationships and proposed IBI metrics that were identified for the Battle River should be applicable beyond this system. Ecological information generated in this study can be used to protect aquatic resources threatened by increasing pressures from human developments and activities in western Canada.

**Acknowledgments**

The authors thank the following individuals, agencies, and corporations for their contributions and assistance in delivering this project. The Alberta Conservation Association (ACA), Alberta Fish and Wildlife Division (AFWD), and Alberta Environment (AE) provided staff expertise. Alberta Sustainable Resource Development (ASRD) provided the electrofishing boat. Special thanks to Jason Blackburn (ACA), Brad Hurkett (ACA), Diana Rung (ACA), Chris Delage (ACA), Jason Cooper (AFWD), and Vance Buchwald (AFWD) who collected field data. Chris Teichreb (AE) secured funding for the project through the provincial “Water for Life Strategy,” acted as liaison with the Battle River Watershed Alliance, and provided input on various water quality components. Thanks to Lorne Fitch (Cows and Fish organization) for his input on riparian shoreline variables. Thanks also to Alastair Franke who coordinated and chaired several meetings that led to the completion of the Battle River IBI field program. The Department of National Defense (CFB Wainwright) and ATCO (Forestburg) provided financial contributions to the project.

**References**


Received: 29 June 2009; accepted: 4 February 2010.
Frequency Analysis as a Tool for Assessing Adverse Conditions During a Massive Fish Kill in the St. Lawrence River, Canada

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2 Ministère des ressources naturelles et de la faune du Québec, Service de la Faune Aquatique, Québec, Canada
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During the summer of 2001, the largest fish kill in the recorded history of the St. Lawrence River occurred. More than 25,000 dead carp were recovered. Preliminary analyses suggested hydroclimatic factors may have triggered the fish kill. Long time series of hydroclimatic variables were available upstream and downstream from the study area. In order to investigate if hydroclimatic conditions were extreme during the summer of 2001, frequency analyses were performed on time series of air and water temperature, water level, and solar radiation. During this period, the daily maximum water temperature was abnormally high (return period of 47 years) relative to other years. Air temperature was also high (return period of 22 years) and water level was very low (return period of 67 years). Results showed that hydroclimatic forcings were acting at two different time scales. First, short-term extremes are more likely to have direct impacts on ecosystems, such as lethal stress caused by oxygen depletion in shallow areas. Long-term extremes have indirect effects, which are more difficult to detect, such as immunosuppression. These results reiterate the importance of water temperature in aquatic habitat, particularly in the present context of global warming and climate change.

Key words: fish kill, water temperature, physiological stress, St. Lawrence River, frequency analysis

Introduction

Water temperature is one of the most fundamental parameters for assessing suitable conditions for fish (Sinokrot et al. 1995; Mohseni et al. 2003; Cooke et al. 2004). Temperature has an important effect on fish life history characteristics such as survival, growth, spawning date and reproduction, egg incubation, habitat selection, distribution, and migration (Mortsch and Quinn 1996; Bergstedt et al. 2003; Brodeur et al. 2004; Cooke et al. 2004; Gillet and Péquin 2006; Ham et al. 2006; Mingelbier et al. 2008). Although water temperature may not always be the direct driving factor or main stressor leading to mortality, it is often an indirect factor involved in a wide number of physical and physiological processes linked to fish mortalities.

Massive fish kills are defined as events that affect a large number of individuals across relatively large aquatic areas. They are often triggered by adverse environmental conditions. This phenomenon may occur in marine or freshwater environments and may involve one or many fish species (Herman and Meyer 1990). Such events may be related to a broad range of factors, such as high population density, spawning stress, reduced food abundance, excessive or sudden water temperature changes, and bacterial or fungal infections (Herman and Meyer 1990; Bartholow 1991; FWC 2006; MDE 2006).

The St. Lawrence River and the Great Lakes have been the site of a number of fish kills of various scales, but related documentation on them is scarce. A review of provincial and federal reports did not reveal any official mention of massive fish kills, until 2001. The fish kill observed during the summer of 2001 may be the largest event of its kind in the last decades or even the past century on the St. Lawrence River (Monette et al. 2006). Most of the mortality observed during the summer of 2001 occurred in the freshwater reaches of the St. Lawrence River between Montréal and Québec City. During the first part of the event, from June 28 to July 5, 8,127 carcasses were found between Sainte-Anne-de-Bellevue and Québec City (Fig. 1). During the second part, July 6 to July 13, 11,397 dead fish were counted in the same reaches but also in the upstream part of Deux-Montagnes Lake and in the Sorel archipelago. Within this stretch of the St. Lawrence River, the distribution of carcasses did not reveal any spatial or temporal correlation, which indicates that dead fish were not originating from one specific area. During the third period, July 14 to July 31, 6,440 carcasses were collected, mostly in the lower reaches of the study area, between Donnacona and Québec.

The bulk of the dead fish collected were carp but other fish were also found, including: Catostomidae, Anguillidae, Acipenseridae, Ictaluridae, Esocidae, Percidae, and Centrarchidae. About 25,000 dead carp (Cyprinus carpio) were collected along the St. Lawrence River (Mingelbier et al. 2001). This is believed to be a conservative estimate because the carp were only recovered in inhabited areas. The dead carp were mainly large adults and no biological sampling was performed on collected carcasses, except for abundance.
Many hypotheses were reviewed by Mingelbier et al. (2001) to explain the massive fish kill of 2001 in the St. Lawrence River. No toxic spills were reported in St. Lawrence River and its tributaries during the summer of 2001. Analyses for heavy metals and other contaminants showed normal concentrations for the period between April and July 2001, which negated the hypothesis of contamination (Mingelbier et al. 2001).

However, spot measurements of water temperatures as high as 34°C were reported in the area of Lake Saint-Pierre (Mingelbier et al. 2001), which is considered very high for most of the fish of the St. Lawrence River. It is important to mention that during the same period, a similar fish die-off occurred in the neighbouring Lake Champlain area (Vermont, U.S.A.), but for other fish species (Mingelbier et al. 2001). This led to the hypothesis that regional environmental factors may have affected a large area at the same time. Adverse hydrometeorological conditions could therefore be a potential cause of mortality.

Surprisingly, carp was the species mostly affected by the conditions during the summer of 2001. Carp is an opportunistic species that can tolerate many adverse conditions, such as high temperatures, low concentrations of dissolved oxygen, and poor water quality, with a lethal temperature limit between 36 and 41°C (Cooper 1987). The spawning period for carp is triggered when spring or early summer water temperature reaches 17°C. Monette et al. (2006), who examined the dead fish, concluded that the ultimate cause of mortality was opportunistic bacterial infection by *Aeromonas hydrophila* and *Flavobacterium sp.* The gills and the other internal organs presented with infections by these bacteria. Moreover, lesions were observed in the digestive system and on the gills. Such type of infection only leads to mortality when the fish present internal lesions. Since these bacteria do not usually lead to mortality when fish are healthy, it is believed that the fish were immunodeficient because of physiological stress that could have been induced by spawning energy demand and by high water temperature.

Environmental conditions (mostly related to the thermal regime) are suspected to be one of the causes (direct or indirect) of mortality. Therefore, this paper investigates the hydroclimatic conditions during the summer of 2001. The objective is to determine whether extreme conditions that may have been conducive to environmental stress for fish occurred. To achieve this objective, historical water and air temperature series as well as solar radiation and water level historical time series were analyzed using frequency analysis for different durations (1 to 41 days). We aimed to verify if those four variables exhibited extreme values during the summer of 2001. Air temperature, solar radiation, and water levels were selected because they are known to have an impact on water temperature. The relation between air temperature and water temperature is well known and used in numerous studies to predict water temperature by regression (Cluis 1972; Crisp and Howson 1982; Jourdonnais et al. 1992; Stefan and Preud’homme 1993;
Caissie et al. 1998; Mohseni and Stefan 1999). Lack of local data precluded the use of such a relationship to model water temperature where mortality occurred. Therefore, the preferred tool to examine the hydroclimatic conditions was frequency analysis of relatively long time series at stations located in the vicinity of the study area. Extremes of different durations (i.e., 1 to 41 days) from May to August were analyzed.

**Material and Methods**

**Study Area**

The St. Lawrence River, located in Québec, is one of the largest rivers in North America. It flows for more than 1,000 km, from the Great Lakes to the Atlantic Ocean (Fig. 1). Its drainage area covers 1,344,200 km², and the mean annual discharge at Sorel is 10,333 m³/s (Morin and Bouchard 2001). The fish kill occurred in the freshwater portion of the St. Lawrence River. The morphology of this section is highly variable. Downstream from Montréal the flow is mainly concentrated in the navigation channel, which has a minimum depth of 12 m and a width of 250 m (Triboulet et al. 1977). The mean width of the section between Montréal and Québec City is about 2.5 km, except in Lake St. Pierre, which is a widening of the river (approximately 15 km in width) where the mean depth is about 3 m. It takes approximately three to four days for water to flow from Montréal to Québec City.

**Data**

The only spot measurements available during the event originated from the monthly water quality data of the Banque de données sur la qualité du milieu aquatique (BQMA) (MDDEP 2008). This routine monitoring was not specifically targeting the fish kill conditions. In 2001, a total of 15 variables were monitored, including chlorophyll \( a \), nitrates and nitrites, total nitrogen, dissolved oxygen, pH, total dissolved and suspended phosphorus, and turbidity. The data are presented in Table 1, but only for the parameters that were measured for the entire summer period. Spot measurements showed no abnormal variation of the water chemistry. However, the sampling frequency (monthly) of this monitoring effort did not permit us to fully assess the prevailing conditions. It should be noted that the temperatures in Table 1 show a maximum value of 24°C at the monitoring station, which is close to the all-time maximum (25°C).

Long-term time series of air and water temperatures as well as water levels and global solar radiation were used to quantify how extreme the meteorological and aquatic conditions were during the summer of 2001. The stations used in this study were selected for their relative proximity to the study area, the length of the time series, and whether the series included 2001 (Table 2).

**Frequency Analysis**

Frequency analyses were performed on temperature (air and water), water level, and solar radiation time series. The daily air temperature ranges, which are the differences between maximum and minimum temperature, were also examined. Frequency analysis is a statistical approach that relates the magnitude of events, e.g., extreme temperature, to a probability of exceedance for a given duration. A return period is calculated based on the probability that the event will be equalled or exceeded in any given year. The return period is defined in equation (1):

\[
T(x_t) = \frac{1}{1 - F(x, \theta)}
\]

where \( T(x_t) \) is the return period associated with a given event, \( x_t \); \( F(x, \theta) \) is the probability distribution of \( x \) with \( n \) observation \( (x = \{x_1, \ldots, x_n\}) \); and \( \theta \) represents the vector of the parameters of the probability distribution \( F \). Hence, a statistical distribution is fitted to annual or seasonal extremes and this model is used to calculate probabilities

---

**TABLE 1.** Spot measurements of water quality variables in 2001 (MDDEP 2008)

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Active chlorophyll ( a ) (mg/L)</td>
<td>3.05</td>
<td>3.35</td>
<td>1.68</td>
<td>1.60</td>
<td>2.37</td>
<td>3.35</td>
<td>1.60</td>
</tr>
<tr>
<td>Aluminum (mg/L)</td>
<td>0.02</td>
<td>0.07</td>
<td>0.06</td>
<td>0.05</td>
<td>0.06</td>
<td>0.07</td>
<td>0.02</td>
</tr>
<tr>
<td>Ammoniacal nitrogen (mg/L)</td>
<td>0.01</td>
<td>0.03</td>
<td>0.06</td>
<td>0.02</td>
<td>0.03</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>247.17</td>
<td>238.33</td>
<td>252.00</td>
<td>264.33</td>
<td>249.59</td>
<td>264.33</td>
<td>238.33</td>
</tr>
<tr>
<td>Dissolved oxygen (mg/L)</td>
<td>10.6</td>
<td>9.49</td>
<td>7.94</td>
<td>8.37</td>
<td>8.93</td>
<td>10.6</td>
<td>7.94</td>
</tr>
<tr>
<td>Fecal coliforms (CFU/100mL)</td>
<td>1,130</td>
<td>3,190</td>
<td>1,490</td>
<td>1,210</td>
<td>1,350</td>
<td>3,190</td>
<td>1,130</td>
</tr>
<tr>
<td>Nitrates and nitrites (mg/L)</td>
<td>0.32</td>
<td>0.36</td>
<td>0.24</td>
<td>0.15</td>
<td>0.28</td>
<td>0.36</td>
<td>0.15</td>
</tr>
<tr>
<td>Organic carbon (mg/L)</td>
<td>3.22</td>
<td>3.67</td>
<td>3.10</td>
<td>3.07</td>
<td>3.16</td>
<td>3.67</td>
<td>3.07</td>
</tr>
<tr>
<td>pH</td>
<td>7.98</td>
<td>8.10</td>
<td>8.22</td>
<td>8.40</td>
<td>8.16</td>
<td>8.40</td>
<td>7.98</td>
</tr>
<tr>
<td>Phoephvlin (mg/m³)</td>
<td>1.15</td>
<td>1.02</td>
<td>0.57</td>
<td>0.78</td>
<td>0.90</td>
<td>1.15</td>
<td>0.57</td>
</tr>
<tr>
<td>Suspensions solids (mg/L)</td>
<td>9.83</td>
<td>6.67</td>
<td>5.83</td>
<td>6.33</td>
<td>6.50</td>
<td>9.83</td>
<td>5.83</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>13.22</td>
<td>19.05</td>
<td>20.65</td>
<td>24.08</td>
<td>19.85</td>
<td>24.08</td>
<td>13.22</td>
</tr>
<tr>
<td>Total dissolved phosphorus (mg/L)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Total suspended phosphorus (mg/L)</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>5.47</td>
<td>3.47</td>
<td>1.63</td>
<td>3.07</td>
<td>3.27</td>
<td>5.47</td>
<td>1.63</td>
</tr>
</tbody>
</table>
of exceedance for different return periods. The complete theory and detailed description of frequency analyses are described in many books, such as Rao and Hamed (2001).

Time series of daily data were extracted and moving averages with different time periods were calculated for the period of interest (May to August). As described earlier, there were strong indications that the 2001 mortality event was directly caused by abnormal meteorological conditions. These peculiar conditions were likely initiated in the weeks prior to the onset of the first mortalities (i.e., the second week of June) and may have lasted for a portion of July, for a total of more than 30 days. However, it is also possible that stressful or lethal temperatures were exceeded for a shorter period, and subsequent mortalities were observed for weeks after, even if temperatures had returned to more normal values. For this reason, moving averages were calculated with duration windows of 1, 3, 7, 15, 31, and 41 days in order to assess the event duration. Frequency analyses were performed on seasonal (May to August) maxima and minima of the times series of moving averages. For temperature minimum, we selected for analysis the highest minimum values because they are indicative of continued potential stressful events (i.e., the temperature remained high throughout the day). With this approach, quantiles for different return periods (e.g., 2, 5, 10, 50, 100 years) and different durations were estimated. Intensity-duration-frequency curves can thus be built to provide graphical representations of the probability that a given event, $x_t$, of a duration of 1 to 41 days will occur (Rao and Hamed 2001; Khaliq et al. 2005; Meylan et al. 2007). Extreme events are quantified in terms of duration and frequency.

Frequency analysis is based on three hypotheses: homogeneity, stationarity, and independence of the time series. The following three statistical tests were used in this study: 1) the Wilcoxon test for homogeneity (Wilcoxon 1945); 2) the Kendall test for stationarity (Mann 1945); and 3) the Wald-Wolfowitz test for randomness (Wald and Wolfowitz 1943).

A total of eight distributions were tested and compared for goodness of fit on each series: four two-parameter and four three-parameter distributions. Each time, the distribution that showed the best fit was chosen to calculate $T(x_t)$. These distributions and their probability density functions are presented in Table 3.

The parameters of each fitted distribution can be estimated using different approaches. In the present study, the maximum likelihood method was used. This method has the advantage of producing the smallest variance in estimating the parameters and the quantiles (Meylan et al. 2007).

The adequacy of the fit of each statistical distribution to the observations was examined using different methods: the Chi-squared test was used to verify the hypothesis that the selected distribution can be considered as the parent distribution of the sample. In addition, the Akaike criterion (AIC) (Akaike 1974) and Bayesian Information Criterion (BIC) (Schwartz 1978) were also used to compare the goodness of fit of different distributions. The distribution with the best fit is the one with the lowest criteria values. The BIC tends to be more severe than the AIC, and generally the BIC is the first selection criterion. All frequency analyses were performed with HYFRAN software.

### Results

#### Time Series Analysis

Correlation between air and water temperatures was calculated for different lags using daily data. It reached maximum values (median of 0.9) for concomitant series (i.e., a lag of 0 between air and water temperature) and decreased with an increasing lag, but remained greater than 0.5 up to a lag of ±2 and greater than 0.4, up to a lag of ±3 (Fig. 2). This suggests that water and air temperatures followed the same temporal pattern, with little delay between the two extremes. Hence, an analysis of air temperature may provide insight into the prevailing water conditions.

The analysis of empirical probabilities for daily air temperature during the period from 1970 to 2000 revealed that the maximum values recorded from early May 2001 (29°C) exceeded the 95th percentile (Mingelbier et al. 2001). Such extreme temperatures occurred during three days in May 2001. Higher maximum values were also recorded twice: in mid-June (33°C; >99%) and late
Adverse Conditions During a Massive Fish Kill

Fig. 2. Box plots of annual correlation coefficients between air temperature (Dorval Airport) and water temperature (Labatt Brewery intake) for different lags; the median value is indicated by a horizontal line inside the box.

June (29°C; >95%). In addition, relatively low daily minimum temperatures were observed in early June, about eight days before the highest daily air temperature maximum peak. Early in May, air temperature at Dorval remained above 28°C for three days. The same pattern was observed in Québec City (Fig. 3).

Water temperature in the upstream portion of the study area remained above 20°C throughout the summer after June 9. Downstream, at the Sainte-Foy pumping station, water temperature reached 20°C by mid-June and remained above this threshold for the rest of the summer (Fig. 4). Spot measurements in June revealed water temperatures as high as 34°C in the Lake Saint-Louis and Lake Saint-Pierre areas (Mingelbier et al. 2001).

During the same period, water levels were constantly decreasing from May to mid-August, exhibiting extremely low values: 4.95 m at the Frontenac station (compared with the interannual mean of 6.35 m for the same period), 3.61 m at the Sorel station (interannual mean = 4.93 m), and 0.51 m for the Neuville station (interannual mean = 1.17 m) (Fig. 5).

### TABLE 3. Probability distribution functions used in the frequency analysis

<table>
<thead>
<tr>
<th>Name</th>
<th>Probability density function</th>
<th>Domain</th>
<th>Number of parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamma</td>
<td>( f(x) = \frac{\alpha^k}{\Gamma(k)} x^{k-1} e^{-\alpha x} )</td>
<td>( x &gt; 0 )</td>
<td>2</td>
</tr>
<tr>
<td>GEV (^a)</td>
<td>( f(x) = \frac{1}{\alpha} \left[ 1 - \frac{k}{\alpha} (x-u)^{-k} \right] \exp \left[ -\left[ 1 - \frac{k}{\alpha} (x-u)^{-k} \right]^{\frac{1}{k}} \right] )</td>
<td>( x &gt; u + u/k ) if ( k&lt;0 ) ( x &lt; u + u/k ) if ( k&gt;0 )</td>
<td>3</td>
</tr>
<tr>
<td>Gumbel</td>
<td>( f(x) = \frac{1}{\alpha} \exp \left[ -\frac{x-u}{\alpha} - \exp \left( \frac{x-u}{\alpha} \right) \right] )</td>
<td>( -\infty &lt; x ) ( x &lt; -\infty )</td>
<td>2</td>
</tr>
<tr>
<td>Log-normal 2 parameters</td>
<td>( f(x) = \frac{1}{x\sigma \sqrt{2\pi}} \exp \left{ -\frac{(\ln x - \mu)^2}{2\sigma^2} \right} )</td>
<td>( x &gt; 0 )</td>
<td>2</td>
</tr>
<tr>
<td>Log-normal 3 parameters</td>
<td>( f(x) = \frac{1}{(x-m)\sigma \sqrt{2\pi}} \exp \left{ -\frac{(\ln(x-m) - \mu \sigma^2)}{2\sigma^2} \right} )</td>
<td>( x &gt; m )</td>
<td>3</td>
</tr>
<tr>
<td>Log-Pearson Type 3</td>
<td>( f(x) = \frac{\alpha^k}{\Gamma(k)} (\ln x - m)^{k-1} e^{-\alpha (\ln x - m)} )</td>
<td>( X &gt; e^m )</td>
<td>3</td>
</tr>
<tr>
<td>Pearson Type 3</td>
<td>( f(x) = \frac{\alpha^k}{\Gamma(k)} (x-m)^{k-1} e^{-\alpha (x-m)} )</td>
<td>( x &gt; m )</td>
<td>3</td>
</tr>
<tr>
<td>Weibull</td>
<td>( f(x) = \frac{c}{\alpha} \left( \frac{x}{\alpha} \right)^{c-1} e^{-\left( \frac{x}{\alpha} \right)^c} )</td>
<td>( x &gt; 0 )</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^a\) GEV = generalized extreme value.

---

**Fig. 2.** Box plots of annual correlation coefficients between air temperature (Dorval Airport) and water temperature (Labatt Brewery intake) for different lags; the median value is indicated by a horizontal line inside the box.
Fig. 3. Air temperatures between May 1 and August 31, 2001 from climatologic stations of (a) Dorval Airport (Montréal) and (b) Québec City Airport.

Fig. 4. Water temperatures between May 1 and August 31, 2001 from water supply installations of the Labatt Brewery (Montréal) and Sainte-Foy.

Fig. 5. Water levels between May 1 and August 31, 2001 from the Frontenac (Montréal), Sorel (Lake Saint-Pierre), and Neuville (near Québec City) stations.

**Frequency Analysis**

All series were tested for homogeneity, stationarity, and independence with a significance level of 0.05. Only one time series, the daily temperature range time series with a duration of 41 days, failed the test of independence and was therefore excluded from the analysis. For the majority of tested series (nine), the most adequate statistical model was a Weibull distribution. The remaining four cases were adjusted with two-parameter log-normal, three-parameter log-normal, gamma, and generalized extreme value (GEV) distributions.

The intensity-duration-frequency (IDF) curves are similar for the Dorval and Québec stations. Therefore, only those for Dorval are presented (Fig. 6 and Fig. 7). Using these IDF curves, it is possible to calculate the return period for 2001 for events of durations of 1, 3, 7, 15, 31, and 41 days. This is presented in Table 4. At Dorval Airport, temperature maximums in 2001 had a high return period for shorter durations (one and three days), with a maximum of 22 years. For longer durations, the return periods decreased slowly to reach a value of 15 years (duration 15 days). The return period for durations of 31 and 41 days are less than two years, showing that the extreme warm event in air temperature lasted between 15 and 31 days. Results for the Québec meteorological station were quite different with almost all T\textsubscript{max} return periods equal to two years or less for 2001. The only exception was for the one-day duration maximum temperature, which had a return period of six years.

Extreme low daily air temperatures were not relevant for this study. High minimum values would indicate that fish were not submitted to colder spells during which they could recuperate from the high maxima. To investigate this hypothesis, frequency analysis was performed on the maximum values of T\textsubscript{min}. For air temperatures, all return
periods for the $T_{\text{max}}$ maxima in 2001 were less than two years for all durations and for both stations.

The IDF curves for the water temperature time series are again presented for only one of the two stations (Labatt) because of similarities in the results (Fig. 8 and Fig. 9). These results were calculated for durations of 1, 3, 7, 15, 31, and 41 days. The return periods for 2001 were extracted from these curves and are summarized in Table 4. For the Labatt station, the return period calculated for the shortest duration was about eight years and increased for longer durations: up to $T(x_t) = 19$ years for an event duration of 15 days and $T(x_t) = 17$ years for durations of 7 and 31 days. The return period decreased to less than two years for the longer (41 days) duration. This confirms that the high water temperatures of the summer of 2001 were not commonly observed. The low return period for the 41 day duration is an indication that the high temperature event was not sustained for such a long interval. At high minimum water temperatures, high return periods for short durations were seen (e.g., a return period of 47 years for a duration of three days); the return period decreased to seven years for a duration greater than 15 days. This indicates that minimum water temperatures were occasionally unusually high during the study period.

For the Sainte-Foy station, the estimated return periods were higher than those of the Labatt station (Table 4). For the shortest duration, the return period was 15 years and increased in duration to a maximum return period of 48 years for a duration of 31 days. When event duration was further increased to 41 days, return periods were found to be lower than two years. This again highlights the fact that the warm event was shorter than 41 days, i.e., the total duration was probably in the order of one month. Minimum temperatures showed similar results, with an event duration of approximately one month and the highest return period for a duration of 15 days (21 years).

For both the Labatt and Sainte-Foy stations, the daily temperature ranges were also examined for the same durations. In all cases the return periods calculated were shorter than two years. It seems that the daily

---

**TABLE 4.** Return period in years computed for the different time series of different durations in days during the summer of 2001$^a$

<table>
<thead>
<tr>
<th>Duration</th>
<th>Dorsal $T_{\text{max}}$</th>
<th>Dorsal $T_{\text{min}}$</th>
<th>Québec $T_{\text{max}}$</th>
<th>Québec $T_{\text{min}}$</th>
<th>Labatt $T_{\text{max}}$</th>
<th>Labatt $T_{\text{min}}$</th>
<th>Sainte-Foy $T_{\text{max}}$</th>
<th>Sainte-Foy $T_{\text{min}}$</th>
<th>Frontenac Level</th>
<th>Sorel Level</th>
<th>Newville Level</th>
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<tr>
<td>1</td>
<td>22</td>
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<td>≤2</td>
<td>8</td>
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<td>15</td>
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<td>≤2</td>
<td>4</td>
<td>≤2</td>
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<td>≤2</td>
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<td>10</td>
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<td>18</td>
<td>20</td>
</tr>
</tbody>
</table>

$^a$ $T_{\text{max}}$ is maximum temperature, $T_{\text{min}}$ is minimum temperature, and water levels are the minimum values.
water temperature ranges were not abnormal. There was an upward shift in all water temperatures, but the difference between the maximums and minimums were not atypical.

For water levels, an example of the IDF curve is shown for the Sorel station (Fig. 10), and information on the exact return periods of the 2001 event is presented in Table 4. For the three stations, Frontenac, Sorel, and Neuville, the return periods calculated for different durations indicate that the event of 2001 was extreme. For the Frontenac (Montréal) water level station, the return period for a five-day duration was 23 years and for a duration of 41 days, it was 13 years (Table 4). The return periods obtained in Lake Saint-Pierre were greater: 31 years for a five-day duration and 18 years for an event duration of 41 days. For the Neuville water level station, the return periods calculated for the same set of durations were, respectively, 46 and 20 years. The tidal signal is present at Neuville. This may explain the return period of 67 years that was calculated for a duration of 15 days since it is possible that the low discharge was associated with the spring fortnightly tidal cycle to produce extremely low levels.

Analysis for global solar radiation (not shown) indicated that the maximum and minimum global solar radiation were normal during the summer of 2001. All of the estimated return periods were less than 5 years. It seems that the high water temperatures observed in 2001 were not the consequence of high radiation inputs associated with long periods of low cloud cover.

**Discussion**

Extremes of hydroclimatic variables can be characterized by frequency analysis which is a useful tool for determining the return period of a specific event. In the present study, results showed that the St. Lawrence River experienced unusually high water temperatures associated with elevated air temperatures and low water levels during the summer of 2001. It is important to mention that these events and the mortality have not only temporal concordance, but also a concordance in the duration of the events; this suggests that there is a link between the extreme hydroclimatic conditions and fish mortality.

Water temperatures in 2001 exhibited abnormal return periods of 47 years for short and long durations; these results are mostly representative of temperatures in the deeper channel. In fact, heating processes differ between the deep and shallow areas. Shallow water areas in the St. Lawrence River, where carp usually spawn in early June, are exposed to rapid heating effects. Hence, it is possible that the extreme values with similar or even greater return periods in shallow water occurred, and that they were associated with higher quantile values.

Similarly, extreme values of air temperatures (maximum return period of 22 years) and water levels (maximum return period of 67 years) occurred during the summer of 2001. Abnormally high air temperatures

![Fig 8. IDF curve for the maximum water temperature of the Labatt Brewery station.](image)

![Fig 9. IDF curve for the minimum water temperature of the Labatt Brewery station.](image)

![Fig 10. IDF curve for the minimum water level at the Sorel station (Lake Saint-Pierre).](image)
Carp are known to be resistant fish, but during the spawning period their resistance to adverse environmental conditions may be lower because most of their energy is used for reproduction activities, which diminishes their ability to fend off infections or other metabolic requirements (Sandström et al. 1997; Beer and Anderson 2001). Moreover, the lethal limit for carp, which is between 36 and 41°C, was nearly reached during the summer of 2001, with the temperature measured at 34°C. There is little literature on the joint effect of bacterial and environmental stressors, and more research on these complex interactions is required to gain better understanding of the processes.

Multiplication of bacteria such as *A. hydrophila* and *Flavobacterium sp.* and the resulting infections are mostly driven by water temperature (Nematollahi et al. 2003). These bacteria are harmful pathogens widely known to impact freshwater fish (Decostere et al. 1999; Suomalainen et al. 2005). In this case, it is hypothesized that infection was spread by frequent contacts between individual fish during spawning. In the case of *Flavobacterium sp.*, a high water temperature increases the growth of the bacteria, facilitates the attachment of the bacteria to gill arches, and the rate of mortality of fish is known to increase when water temperature rises, which may result in up to 100% mortality at temperatures above 20°C (Suomalainen et al. 2005). The mortality rate with *A. hydrophila* could be greater because this bacterium has the possibility of producing a number of potential virulence factors, including cytotoxin, haemolysin, and enterotoxin. The optimal temperature for the growth of this bacterium is 30°C (Sautour et al. 2003). Such extreme high water temperatures were observed in some areas of the St. Lawrence River during the summer of 2001.

**Conclusion**

Frequency analysis indicated, through high return periods for water temperature and water levels, that the summer of 2001 was subjected to abnormal events that only occur once in more than thirty years on average. Moreover, these extreme events were concomitant with fish mortality. High temperature events had similar durations as the mortality event, i.e., a maximum of 31 days and a probable mean close to 15 days. The available data on air and water temperature as well as water levels suggested that this particular fish kill was most likely driven by hydroclimatic conditions, and that the thermal conditions caused high stress; this may have been a sufficient factor for potential mortality.

It is suspected that carp were mostly affected because they are one of the species that reproduce the latest in the spring. Also, they only spawn once a year and therefore invest much more energy in single seasonal reproduction than multiple spawners do. Energy and oxygen expenditures are also more important for large fish, which may explain why carp were more affected by such drastic changes in abiotic variables than other fish species that may have been using similar habitat during this period.
Massive fish kills have great impacts on the ecosystem and on the economy. For the aquatic ecosystem, a massive fish kill such as the event of 2001 in the St. Lawrence River has led to a loss of perhaps more than one cohort for a species (carp) and perhaps other species as well. This could have many impacts on the food web. Impacts for the ecosystem can be catastrophic if dead fish are not recovered. Decomposing carcasses could be a vector of diseases or lead to a temporary depletion of oxygen as a consequence of the decomposition. When the species affected is an economically important species, the consequences can be disastrous for fisheries. The massive depletion of fish biomass can lead to poor captures for many years, depending on ecosystem recovery time. It is therefore important to study fish kills in order to understand the phenomena that could lead to such events and attempt to prevent them or mitigate their impacts.

It is possible that in the future, hydroclimatic conditions such as those observed during the summer of 2001 will occur more frequently or during other periods of the year. Therefore, it is important to increase our knowledge on how future water temperature changes could affect fish and lead to mortality. But also, there is a need for further investigations into the role of thermal refugia for fish adaptation and survival. Numerous questions can be raised on the use of thermal refugia by fish with respect to the definition of threshold temperatures, their location, and how fish use them. There is also a need to have a better understanding of processes occurring in shallow water, where fish spawn. Moreover, this study also highlights the importance of gaining a better understanding of combined stressors on organisms like fish. In the case studied here, neither spawning nor water temperature alone could have led to a massive fish kill. Rather, it appears that the high mortality was the result of the combined effects and that water temperature was a driving factor. These interactions are complex and need to be thoroughly studied in the future.

Some answers may be provided by developing and using spatially explicit habitat models, which can link biological, physical, and hydrological variables. These are useful tools to understand the spatiotemporal variability of such habitat characteristics, and there is a need to implement them in the context of climate change.

Acknowledgments

The authors are indebted to P. Gachon (Environment Canada) for providing insightful advice and facilitating meteorological data acquisition. Funding for this project was provided by FQRNT, NSERC, Environment Canada, and Québec's Department of the Ministry of Natural Resources and Wildlife.

References


Adverse Conditions During a Massive Fish Kill


Received: 16 December 2008; accepted: 16 October 2009.
GDVFS: A New Toolkit for Analysis and Design of Vegetative Filter Strips Using VFSMOD

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The Guelph design tool for vegetative filter strips, GDVFS, is a toolkit for the analysis and design of vegetative filter strips (VFSs). The upland hydrology model UH and the vegetative filter strip model VFSMOD (the two main components of GDVFS) were adopted from an existing interface (VFSMOD-W), and new nutrient and bacteria transport add-ons for UH and VFSMOD were incorporated into GDVFS. Other utilities and tools were also included in GDVFS to provide a capable toolkit for the analysis and design of VFSs. The published evaluation of computational procedures used in GDVFS indicates that these procedures perform very well in the estimation of VFS sediment and phosphorus removal efficiencies. According to these results, comparison of the predicted and observed values for sediment and phosphorus removal efficiencies indicates 10 and 20% error, respectively. This paper provides descriptions on the capabilities and methodology followed in the GDVFS toolkit.

Key words: vegetative filter strip, design tool, nonpoint source pollution control, stormwater management

Introduction

Runoff generated in a hillslope catchment, which carries sediment-bound and dissolved pollutants, enters the watershed stream network through flow paths perpendicular to the stream segments. A strip of dense vegetation called a vegetative filter strip (VFS) constructed at the downstream edge of the field within the buffer zone of a stream segment can effectively reduce the pollution of the stream by i) trapping the sediment and therefore sediment-bound pollutants carried in the surface runoff through particle settlement mechanism within the vegetated strip, and ii) facilitating the infiltration of the surface flow containing dissolved pollutants.

To design and evaluate VFSs, generally based upon mass removal of sediment, Munoz-Carpena et al. (1999) developed the vegetative filter strip model VFSMOD. To improve the capabilities of VFSMOD, the Guelph design tool for VFSs, GDVFS, was developed by the authors to provide a new interface linked with nutrient and bacteria yield and transport models.

GDVFS was developed in two phases. The first phase mainly focused on adding phosphorus transport components based on the results obtained from field experiments, and the second phase focused on incorporating bacteria transport components.

Background on the Development of GDVFS

Early works on development of the vegetative filter strip model were initiated at the University of Kentucky. Barfield et al. (1979), Tollner et al. (1976, 1977), and Hayes et al. (1984) developed the GRASSF model for filtration of suspended solids by grass filter strips. Wilson et al. (1981) modified and incorporated GRASSF into SEDIMOT II, a hydrology and sediment transport model for mined areas. Munoz-Carpena et al. (1999) incorporated a field-scale upland hydrology model (the UH model) along with VFSMOD, a modified version of GRASSF, in a user interface called VFSMOD-W (IFAS 2010). The capabilities of the graphical user interface and the online support services of VFSMOD-W contributed to the popularity of this public-domain toolkit.

The hydrology and the sediment transport components of VFSMOD-W were retained in GDVFS without any change, and new phosphorus and bacteria yield and transport components as well as tools to facilitate the data preparation and visualization of the model outputs were included in the current version of GDVFS. The performance of the phosphorus and bacteria transport components were evaluated using the data obtained from several field experiments conducted on VFSs.

General Description of GDVFS Computation Procedures

Hydrology and Sediment Transport Model

To estimate runoff and sediment flow at the downstream end of a field, which is the most effective location to construct VFSs, the UH model was adopted from the VFSMOD-W interface. Upland is the field upstream of the VFS, and the inflow to the VFS is the runoff carrying sediment generated within the upland area. The UH model employs methodologies that have been the subject of much research and have been extensively evaluated during the last four decades.
The UH model estimates the runoff hydrograph using the SCS method developed by the U.S. Soil Conservation Service based on a set of modelling parameters, including soil texture, land cover, total rainfall depth, storm pattern and duration, and geometry of the upland field.

The sedimentation process considered in the UH model consists of soil erosion and sediment transport and deposition. The Universal Soil Loss Equation (USLE) (Wischmeier and Smith 1978) is used to estimate the long-term average annual rate of sheet and rill erosion based on rainfall pattern, soil erodibility, field topography, land cover, and support management practices. To estimate sediment yield at the outlet of the upland field (downstream end of a field) for a single rainfall event, the modified version of the USLE, MUSLE (Williams and Berndt 1977), is used in the UH model. In this approach, the sediment yield estimates are based on the total runoff volume, peak runoff rate, and the soil, landuse, topographic, and support management parameters of the USLE.

To add phosphorus and bacteria yield and transport components to the UH model, additional procedures were incorporated in GDVFS to determine the amount of phosphorus and bacteria attached to the eroded soil at the point of detachment and at the field outlet, as well as the portion that is nonattached to the particles and transported by runoff.

**Upland phosphorus yield and transport component (UH_P).** Phosphorus enters a VFS in particulate (attached to the surface of the eroded sediment particles) and soluble (in solution) form. The sediment eroded from upland agricultural fields has more sediment-bound phosphorus per unit weight at the field outlet compared with the topsoil in the upland source area since the large particles, which constitute the major portion of the weight of the eroded soil, would settle prior to reaching the field outlet. This is due to the selective processes of erosion and transportation of the fine soil particles. To estimate the sediment-bound phosphorus losses from the upland agricultural fields, an algorithm similar to the one used in the CREAMS model (Knisel 1980) has been adopted in the upland phosphorus yield and transport component of GDVFS (UH_P). In this approach, the specific surface area of the eroded sediment particles at the field outlet is estimated and the amount of phosphorus attached to the sediment particles is computed using the concept of enrichment ratio. The amount of phosphorus transported by the eroded sediment is estimated using the following equation:

\[ SEDP = SOILP \times SED \times PER \]  

where \( SEDP \) is the amount of particulate P transported with surface runoff (kg of P per ha); \( SOILP \) is the P content in the upland field (kg of P per kg of soil) in the top 10 mm of soil surface layer; \( SED \) is the amount of soil loss from upland area (kg/ha); and \( PER \) is the phosphorus enrichment ratio.

\( PER \) is defined as the ratio of the specific surface area of the sediment at the field outlet to the specific surface area of the eroded soil at the point of detachment that can be estimated knowing the aggregate size distribution of the eroded soil at the point of detachment and the particle size distribution of the sediment at the field outlet.

An approach proposed by Foster et al. (1985) was adopted to estimate the aggregate size distribution of the eroded soil at the point of detachment (clay, silt, sand, small aggregates, and large aggregates). In this approach, the aggregate size distribution of the eroded upland soil is estimated from the fraction of primary soil particles (clay, silt, and sand) by using the following empirical equations:

\[ ORcl = 0.26PRcl \]  
\[ ORsa = PRsa(1 – PRcl)^2 \]  
\[ ORsg = 1.8PRcl \] (when \( PRcl < 0.25 \))  
\[ ORsg = -0.6(PRcl - 0.25) + 0.45 \] (when \( 0.25 \leq PRcl \leq 0.50 \))  
\[ ORsg = 0.6PRcl \] (when \( PRcl > 0.50 \))  
\[ ORsi = PRsi - ORsg \]  
\[ ORlg = 1 - (ORcl + ORsi + ORsa + ORsg) \]

In equations 2 to 8, the \( PR \) prefix represents the fraction of primary particle classes in the upland soil (clay, silt, and sand), and the \( OR \) prefix represents the fraction of each particle class in the eroded soil at the point of detachment (clay, silt, sand, small aggregate, and large aggregate). This approach has been experimentally evaluated by Meyer et al. (1992).

A computational procedure was also added to GDVFS to estimate the particle size distribution of the sediment at the field outlet based on the aggregate size distribution of the eroded soil at the point of detachment. The following routing function, developed and evaluated by Williams (1980), was used in GDVFS:

\[ \omega_{oi} = \omega_i e^{-\beta \sqrt{d_i}} \]

\( \frac{q_p}{Q_p} \)

where \( \omega_{oi} \) is the portion of particle size \( d_i \) contained in the sediment; \( \omega_i \) is the portion of particle size \( d_i \) contained in the soil; \( q_p \) is the peak runoff rate at the outlet of the source area; \( Q_p \) is the peak rate of rainfall excess; and \( \beta \) is a routing coefficient defined as:

\[ \beta = \frac{-\ln\left(\frac{q_p}{Q_p}\right)^{0.56}}{4.47} \]

To estimate soluble phosphorus entering the VFS, GDVFS uses a methodology suggested by Sharpley et al. (1981). In this approach, the average dissolved phosphorus concentration in the storm runoff (mg/L) is estimated by the following equation:

$$P_d = \frac{K P_0 EDI \rho_b t^a W^b}{V}$$

(11)

where $P_d$ is the amount of phosphorus desorbed into runoff from soil in time $t$ (mg of P per L); $P_0$ is the initial amount of available phosphorus present in the soil (mg of P per g of soil) estimated using a P extraction technique; $EDI$ is the effective depth of interaction between the soil and the surface runoff (cm) and is defined as the thickness of the surface layer of soil (usually 1 cm) which interacts with rainfall and runoff; $\rho_b$ is the bulk density of the soil (g/cm$^3$); $t$ is the desorption reaction duration (min); $W$ is the water-soil ratio (cm$^3$/g); $V$ is the runoff volume during the storm event (cm$^3$); and $K$, $a$, and $b$ are constants for a given soil.

**Evaluation of UH_P.** Performance of the upland phosphorus yield and transport module (UH_P) for particulate P was evaluated using the experimental data reported by Rudra et al. (1985). These data, which were collected during the 1971 to 1975 period, were used for validation of the UH and UH_P models. These experimental data were collected from four plots (plots 3, 4, 7, and 8) that measured 44.2 x 6.4 m with a relatively uniform slope of 8.2, 8.4, 8.8, and 8.9%, respectively, along the length. These plots were situated in the southwest corner of the University of Guelph campus in Ontario (approximate latitude/longitude of 43.527, -80.225). Event-based data (rainfall, total runoff amount, sediment yield, and particulate P) and land surface environment data including soil, landuse, and manure application for a nonsnow period of five years (1971 to 1975), were used for this study. The soil on the plots was Guelph loam (well drained loamy soil with hydrologic soil group B), and the land use for all plots during the 1971 to 1975 period was continuous corn. The land management practices on plots 3 and 7 included stover left on the surface, no tillage, and no manure application. For plots 4 and 8, the management practices included stover removed, fall plowed, and manure application. The initial concentration of phosphorus in the top 1-cm layer of the soil on these plots was 1.85 ppm (Bray-extraction method). The liquid poultry manure application rate along with P content and application schedule on each plot during the testing period is given in Table 1.

The UH and UH_P models were calibrated by comparing computed event runoff (mm), soil loss (t/ha), and particulate P yield (kg/ha) with the observed experimental data for plots 3 and 4. The calibration was performed by adjusting the sensitive parameters to obtain a minimum sum of square error between the computed and observed runoff and particulate P loads for selected events. The comparison focused on nonsnow months from May through October. The calibrated models were validated using the data from plots 7 and 8 for the same events used in the calibration. The calibration and validation results are presented in Tables 2 and 3, respectively. These results are similar to the results obtained by Rudra et al. (1985) by application of the field-scale model CREAMS on the plots. This is due to the piggyback nature of the particulate P on sediment, and sediment on runoff. Any error introduced in the estimation of runoff results in the magnification of errors in the estimation of sediment load and particulate P loads. The UH model standard error of prediction was 3.8 t/ha (41%) for sediment and 2.8 t/ha (46%) for phosphorus, similar to the CREAMS results reported by Rudra et al. (1985).

**Upland bacteria transport component.** Similar to phosphorus, bacteria entering the VFS was divided into particulate-bound (attached to the surface of the sediment particles) and free-floating bacteria. A procedure was added to GDVFS to estimate bacteria applied in the upland area with the assumption that the manure application was uniform over the upland area and the bacteria from the manure was uniformly distributed over the entire upland surface. With these assumptions, the total number of bacteria over the entire area, in colony forming units (CFU), is equal to the rate at which the manure is applied over the area (kg/ha) multiplied by the concentration of bacteria in CFU per kilogram. This computation, along with the computation of bacteria die-off, is done on a daily basis. From the total amount of bacteria applied, the upland bacteria transport component of GDVFS divides the bacteria into two fractions: bacteria in water (free-floating/soluble) and bacteria on the sediment (particulate). To quantify these fractions, the following empirical equations for the retention coefficient or partitioning coefficient developed by Burge and Enkiri (1978), Reddy et al. (1981), and Ling et al. (2002) were used:
Rudra et al.

TABLE 2. Comparison of observed and computed runoff depth, soil loss, and particulate P content for major rainfall events used for calibration of GDVFS upland phosphorus yield and transport module (UH_P)

<table>
<thead>
<tr>
<th>Plot number</th>
<th>Event date (month dd, yy)</th>
<th>Runoff (mm)</th>
<th>Soil loss (t/ha)</th>
<th>Particulate P (kg/ha)</th>
<th>Runoff (mm)</th>
<th>Soil loss (t/ha)</th>
<th>Particulate P (kg/ha)</th>
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<td>6.11</td>
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<td></td>
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<td>9.1</td>
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<td>2.80</td>
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</tbody>
</table>

TABLE 3. Comparison of observed and computed runoff depth, soil loss and particulate P content for major rainfall events used for validation of GDVFS upland phosphorus yield and transport module (UH_P)

<table>
<thead>
<tr>
<th>Plot number</th>
<th>Event date (month dd, yy)</th>
<th>Runoff (mm)</th>
<th>Soil loss (t/ha)</th>
<th>Particulate P (kg/ha)</th>
<th>Runoff (mm)</th>
<th>Soil loss (t/ha)</th>
<th>Particulate P (kg/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plot 7</td>
<td>June 13, 71</td>
<td>16.2</td>
<td>9.70</td>
<td>3.14</td>
<td>13.4</td>
<td>6.84</td>
<td>5.87</td>
</tr>
<tr>
<td></td>
<td>July 26, 71</td>
<td>7.0</td>
<td>2.25</td>
<td>0.67</td>
<td>9.6</td>
<td>4.16</td>
<td>3.83</td>
</tr>
<tr>
<td></td>
<td>August 26, 71</td>
<td>7.4</td>
<td>0.75</td>
<td>0.59</td>
<td>7.8</td>
<td>3.25</td>
<td>3.10</td>
</tr>
<tr>
<td></td>
<td>May 16, 74</td>
<td>15.5</td>
<td>5.26</td>
<td>8.96</td>
<td>13.7</td>
<td>6.16</td>
<td>5.17</td>
</tr>
<tr>
<td></td>
<td>June 19, 75</td>
<td>1.3</td>
<td>0.15</td>
<td>0.39</td>
<td>2.1</td>
<td>0.61</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>August 23, 75</td>
<td>6.6</td>
<td>1.53</td>
<td>2.24</td>
<td>12.3</td>
<td>5.02</td>
<td>4.74</td>
</tr>
<tr>
<td>Plot 8</td>
<td>June 13, 71</td>
<td>12.2</td>
<td>33.16</td>
<td>6.05</td>
<td>13.4</td>
<td>10.45</td>
<td>8.45</td>
</tr>
<tr>
<td></td>
<td>July 26, 71</td>
<td>5.1</td>
<td>4.58</td>
<td>2.02</td>
<td>17.3</td>
<td>13.33</td>
<td>10.42</td>
</tr>
<tr>
<td></td>
<td>August 26, 71</td>
<td>2.5</td>
<td>1.63</td>
<td>0.43</td>
<td>7.8</td>
<td>4.97</td>
<td>4.46</td>
</tr>
<tr>
<td></td>
<td>May 16, 74</td>
<td>19.9</td>
<td>13.83</td>
<td>30.15</td>
<td>20.3</td>
<td>15.56</td>
<td>11.48</td>
</tr>
<tr>
<td></td>
<td>June 19, 75</td>
<td>6.4</td>
<td>8.02</td>
<td>8.69</td>
<td>6.6</td>
<td>4.58</td>
<td>4.39</td>
</tr>
<tr>
<td></td>
<td>August 23, 75</td>
<td>18.8</td>
<td>23.33</td>
<td>11.46</td>
<td>20.2</td>
<td>14.71</td>
<td>11.96</td>
</tr>
</tbody>
</table>

Method 1. (Burge and Enkiri 1978):

\[ K_r = 1.1475(SA) - 64.11 \left( R^2 = 0.6438 \right) \text{ (when } SA \geq 43.5 \)
\[ K_r = 0 \text{ (when } SA < 43.5 \) \)


\[ K_r = 2.445(SA) - 72.72 \; ; \left( R^2 = 0.97 \right) \text{ (when } SA \geq 29.7 \)
\[ K_r = 0 \text{ (when } SA \leq 29.7 \) \)

Method 3. (Ling et al. 2002):

\[ K_r = e^{3.9\ln(C_y)} - 11.3 \; \left( R^2 = 0.67 \right) \)

Method 4. (Ling et al. 2002):

\[ PC = 50.5 \ln(C_y) - 102.2 \; \left( R^2 = 0.89 \right) \)

where \( K_r \) is the retention coefficient (mL/g); SA is the soil surface area (m²/g); \( C_y \) is the clay content of the soil (%); and \( PC \) is the partitioning coefficient with regards to soil adsorption (%).

An approach similar to the one used in the UH-P was used to determine the specific surface area of the eroded sediment particles, bacteria enrichment ratio, and the bacteria attached to the sediment.

Vegetative Filter Strip Model

To evaluate the performance of a VFS for trapping sediment and nutrients entering the VFS from the upland field, the model called VFSMOD (Munoz-Carpena et al. 1999) was adopted and incorporated in GDVFS.
VFSMOD employs the finite element approach to simulate the movement of runoff within the vegetative filter strip. A one-dimensional solution to the kinematic wave approximation of overland flow (conservation of mass and conservation of momentum) is linked to a sediment filtration model to simulate the transport and deposition of sediment based on the hydraulics of flow within the grass media. The VFS parameters consist of soil and vegetation characteristics governing the infiltration, overland flow, and sediment transport and deposition within the VFS. VFSMOD requires a runoff hydrograph for a rain event as the input to the VFS. GDVFS receives the outputs from the UH model to extract incoming sediment characteristics, storm hyetograph, and upland area storm runoff hydrograph, and generates the input dataset for the VFSMOD model.

**Evaluation of VFSMOD.** VFSMOD was evaluated using field experiment data collected during the period of 1998 to 2004 at the University of Guelph in Ontario. Field experiments were conducted in the summer of 1998 in the Carol Creek watershed near Elora, Ontario, during the summer of 2000 at the Guelph Turf Grass Institute and Environmental Research Centre, Guelph, Ontario, and during the summers of 2003 and 2004 at the Elora Research Farm of the University of Guelph. Six types of vegetation cover tested include:

- **Type A.** An equal mixture of perennial ryegrass (*Lolium perenne* L.), Kentucky bluegrass (*Poa pratensis* L.) and reed canarygrass (*Phalaris arundinacea* L.);
- **Type B.** A mixture of birdsfoot trefoil (*Lotus corniculatus* L.) and creeping red fescue (*Festuca rubra*);
- **Type C.** Existing native vegetation, undisturbed for many years, consisting of native species (identity approximated) including wild oat (*Chasmanthium latifolium*), quackgrass (*Elytrigia repens*), tall fescue grass (*Festuca arundinacea*), and dandelions (*Taraxacum officinale*);
- **Type D.** Perennial ryegrass (*Lolium perenne* L.);
- **Type E.** An equal mixture of perennial ryegrass (*Lolium perenne* L.) and red clover (*Trifolium pratense* L.); and
- **Type F.** Kentucky bluegrass (*Poa pratensis* L.).


The comparison of the model-predicted sediment removal efficiency with the observed values collected from 20 filters with varying length, slope, and vegetation cover showed that the slope and intercept of the linear regression lines between predicted versus observed infiltration amounts and sediment removal efficiency were not significantly different from one and zero, respectively, at the 95% probability level (Abu-Zreig et al. 2001).

**VFS Phosphorus Transport Component (VFS_P).** The developed UH_P module generates the required inputs from the upland area for VFSMOD as well as the VFS_P. The phosphorus removal mechanism considered in VFS_P consists of two components: 1) removal due to the settlement of sediment particles and the phosphorus attached to them within the VFS, and 2) removal due to infiltration of water carrying soluble phosphorus as well as fine suspended particles with particulate phosphorus attached to them.

Particulate phosphorus is attached to the surface of sediment particles and the total amount of particulate phosphorus is proportional with the total surface area of the sediment particles. Therefore, the phosphorus removal efficiency is the ratio of the total surface area of the sediment trapped by the VFS to the total surface area of the inflow sediment. The phosphorus enrichment ratio concept, defined as the ratio of the specific surface area of the sediment particles at the VFS outlet to the specific surface area of the sediment particles entering the VFS at the field outlet, was used to quantify the fraction of particulate phosphorus in the sediment exiting the VFS. Using the phosphorus enrichment ratio and the sediment removal efficiency (the ratio of the total amount of sediment trapped by the VFS to total amount of inflow sediment) computed in the sediment transport module, the sediment-bound phosphorus removal efficiency of the VFS is calculated as:

\[
PRE = 1 - \frac{PRE}{SRE} \times (1 - SRE)
\]

Substituting equation 13 and 14 into 16:

\[
PRE = 1 - PER \times (1 - SRE)
\]

where \(PRE\) is the phosphorus removal efficiency; \(PER\) is the phosphorus enrichment ratio for the VFS; and \(SRE\) is the sediment removal efficiency of the VFS.
et al. (2000, 2001a), the following relationship was developed between the VFS \( \text{PER} \) and the \( d_{50} \) of the sediments entering the VFS (\( r^2 = 0.72 \)):

\[
\text{PER} = 0.05 \; d_{50} + 0.85
\]  

(21)

where \( \text{PER} \) is the VFS phosphorus enrichment ratio, and \( d_{50} \) is the median sediment particle size entering the VFS (mm). The empirical equation derived for the VFS phosphorus enrichment ratio (equation 21) includes the removal due to infiltration of the suspended fine particles.

For each set of experimental data, GDVFS was calibrated to satisfy the water balance within the VFS (total runoff entering the VFS, total runoff leaving the VFS, infiltration within the VFS) followed by the sediment and phosphorus removal efficiencies. The model prediction standard error for the phosphorus removal efficiency was less than 15\% (Fig. 1). To include phosphorus removal due to the infiltration of water carrying soluble phosphorus, the water balance within the VFS was carefully satisfied and the removal efficiency was estimated based on the comparison between the total amount of soluble phosphorus entering and leaving the VFS.

**VFS bacteria transport component (VFS \text{B}).** The VFS \text{B} of GDVFS is somewhat similar to the VFS phosphorus transport module described earlier. The additional processes included in VFS \text{B} are the adsorption of bacteria to the vegetation surface and the change in bacteria concentration due to resuspension. The specific surface area approach used to calculate the particle-attached bacteria lost in the VFS was adopted from Rudra et al. (2002). Similar to VFS \text{P}, and based on the concept of the particulate phosphorus enrichment ratio discussed earlier and the sediment removal efficiency calculated in the sediment transport module, the sediment-bound bacteria removal efficiency in the VFS was calculated using the following equation:

\[
\text{BRE} = 1 - \text{BER} \times (1 - \text{SRE})
\]  

(22)

where \( \text{BRE} \) is the bacteria removal efficiency; \( \text{BER} \) is the bacteria enrichment ratio for the VFS; and \( \text{SRE} \) is the sediment removal efficiency of the VFS. The amount of particle-attached bacteria adsorbed to vegetation is computed using an adsorption capacity of the VFS approach outlined by Newham et al. (2005).

Similar to the VFS phosphorus transport component, water balance within the VFS was carefully satisfied to include the bacteria removal due to infiltration of water carrying bacteria nonattached to the particles. The bacterial removal efficiency was estimated based on the comparison between the total amount of bacteria nonattached to the particles entering and leaving the VFS. To quantify the amount of particle-attached (i.e., particle size > 50μm) resuspended bacteria, the approach suggested by Tian et al. (2002) was adopted. According to this approach the bacteria resuspension rate for the settled particle-attached bacteria was computed by the following equation:

\[
R = 1 - e^{-\left(\frac{V_0 - V}{S}\right)}
\]  

(23)

where \( R \) is the daily resuspension rate; \( V \) is the outflow volume; \( V_0 \) is the threshold volume; and \( S \) is the parameter controlling the resuspension.

The developed approach for bacteria (Escherichia coli) removal by VFS was evaluated using the field experimental data collected by Clarke (2007) and Moharir (2007). These experiments focused on the effect of vegetation (Kentucky bluegrass, perennial ryegrass, and mixed sod), filter strip lengths (5, 10, and 15 m), and inflow rates (0.5, 1.0, and 1.5 L/s) on bacteria removal. This data set was randomly partitioned into two groups; one set was used for calibration of the developed algorithm and the second for the validation. The observed and modelled results show a bacterial removal efficiency of 69\% for the suspended bacteria and 98\% for the particle-attached bacteria transported through the VFS (Moharir 2007).

**Overview of the GDVFS Interface**

GDVFS is a graphical user interface for the two main components, the UH and VFSMOD models, and the corresponding phosphorus and bacteria transport submodels. The modelling concept used in the GDVFS components is categorized as event-based since the entire simulation is performed based on a single rain event. Input parameters are introduced to GDVFS in the form of a “project,” and each project folder has a standard subfolder structure in which the project data files are...
stored. GDVFS is capable of generating and storing scenarios for major computation modules for future access. Some basic tools are also provided in GDVFS, which help the user to evaluate the outputs or directly access and modify the input files within the GDVFS environment.

Application of GDVFS in Simulation Mode

GDVFS can be used in simulation mode to evaluate the performance of an existing VFS. To simulate the hydrological processes, GDVFS requires rainfall depth, storm duration, and a standard rainfall pattern, characteristic of an event-based model, as input parameters. The modelling concept used in GDVFS to estimate erosion and sediment yield is essentially proposed for a field-size upland area, although the same concept is widely used by other sediment transport models regardless of the size of the upland area.

In simulation mode (Fig. 2), sediment, phosphorus, and bacteria movement within the upland field and the VFS are simulated using input parameters provided by the user. In this mode, the user provides all the input data for a given scenario. The online help included in the GDVFS data entry forms assists users to specify the simulation parameters. The structure of the simulation mode helps users to prepare the input data and run the program in a proper sequence. A set of default parameters has been included in some data entry forms, which can be used to setup the input dataset using predefined parameters. The default parameters can be modified and stored by the user for further use to generate or modify other scenarios.

The list of the input parameters for the UH model is given below:

- Total area of upland field (ha)
- Flow path length (m)
- Average flow path slope (%)
- Soil texture
- NRCS (Natural Resources Conservation Service) curve number
- USLE crop factor
- USLE practice support factor
- Total rainfall depth (mm)
- Storm duration (hours)
- Synthetic rainfall pattern (SCS)

The results of the UH model along with the user-defined VFSMOD parameters are used to simulate the VFS. The VFSMOD input parameters are as follows:

![Fig. 2. GDVFS simulation steps.](image)
Fig. 3. Data preparation for the application of GDVFS in design mode.

- Vegetation parameters
  - Spacing of the filter media elements (cm)
  - Filter media (grass) Manning’s n
  - Filter media height (cm)
  - Bare surface Manning’s n
- Overland flow parameters
  - Width of the filter strip (m)
  - Filter length in flow direction (m)
- Infiltration soil parameters
  - Saturated hydraulic conductivity, \( K_s \) (mm/h)
  - Green-Ampt’s average suction at wetting front (mm)
  - Saturated soil-water content, \( \theta_s \) (m³/m³)
  - Initial soil-water content, \( \theta_i \) (m³/m³)
  - Maximum surface storage (mm)
- Incoming sediment characteristics
  - Portion of incoming sediment with diameter >37 μm
  - Incoming flow sediment concentration (g/L)
  - Porosity of deposited sediment (ratio)
  - Sediment particle size, diameter \( d_{50} \) (μm)
  - Sediment particle density (g/cm³)

Application of GDVFS in Design Mode

When used in design mode (Fig. 3) for a set of known parameters, GDVFS executes the computational modules iteratively to size the filter strip to satisfy a user-defined criterion. An independent variable specific to the site is selected by the user from geometrical and topographic characteristics of the upland area, total rainfall, rainfall duration, the USLE crop management factor, the USLE soil erodibility factor, the USLE practice support factor, and the quantity of applied fertilizer and/or manure. The criterion is selected from sediment concentration, phosphorus concentration, total sediment, total phosphorus, sediment removal efficiency, phosphorus removal efficiency, and bacteria removal efficiency.

In the example shown in Fig. 4, the total rainfall was set as an independent variable, filter geometry (length) was set as an unknown dependent variable, and sediment removal efficiency equal to 80% was set as criterion. GDVFS executes the vegetative filter strip model iteratively to satisfy the specified criterion for each computation step within the independent variable.
domain specified by the user (in this example total rainfall was changed from 40 to 80 mm).

Figure 5 shows an example of another application of GDVFS in design mode, which can be used to determine the VFS outflow characteristics (sediment concentration, phosphorus concentration, total sediment, total phosphorus, sediment removal efficiency, and phosphorus removal efficiency) with the variation of the VFS geometry (filter length).

Summary

The UH component of GDVFS simulates the quantity and quality of runoff from the upland area entering the VFS. The VFSMOD component simulates the transport of runoff and sediments through the VFS. The upland phosphorus and bacteria transport components of GDVFS are used to estimate the amount of phosphorus and bacteria initially available within the upland field, and to break down the sediment yield from the upland field into particle size classes. The soluble and particulate phosphorus and bacteria entering the VFS are removed mostly through the infiltration and sediment deposition mechanisms in the VFS. The output of VFSMOD is used to estimate the removal efficiency of the VFS for sediment, phosphorus, and bacteria. The VFSMOD component also estimates the amount of infiltration along the length of the VFS, the dominant mechanism responsible for trapping suspended bacteria and soluble phosphorus.

The developed GDVFS toolkit can be used for site specific design of VFSs to control nonpoint source pollution and to evaluate the performance of existing filter strips based on the characteristics of the upland area contributing to the VFS.

References


Received: 24 March 2009; accepted: 25 September 2009.
Contaminant Trends in Suspended Sediments in the Detroit River-Lake St. Clair-St. Clair River Corridor, 2000 to 2004

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Environment Canada, 867 Lakeshore Road, Burlington, ON L7R 4A6 Canada

Suspended sediments from the Detroit River-Lake St. Clair-St. Clair River corridor over the period of 2000 to 2004 were analyzed to examine the spatial distributions of contaminants including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and mercury. Contaminant spatial distributions were similar over the five-year study period, but concentrations varied considerably among sampling locations. Concentrations of PCBs ranged from 22 to 1,200 ng/g (dry weight) in 2004, and from 10 to 2,700 ng/g (dry weight) in 2000; concentrations of PAHs ranged from 640 to 52,000 ng/g (dry weight) in 2004, and from 240 to 82,000 ng/g (dry weight) in 2000; and concentrations of mercury ranged from 0.063 to 0.478 mg/kg (dry weight) in 2004, and from 0.060 to 0.514 mg/kg (dry weight) in 2002. The highest PCB and PAH concentrations were associated with suspended sediments in the lower and middle reaches of the Detroit River in the area of the Trenton Channel, and the outflow of the Rouge River. The spatial distributions of mercury were more consistent throughout the entire corridor, indicating the presence of sources in both the lower reaches of the Detroit River and the upper reaches of the St. Clair River. Both the Trenton Channel area of the Detroit River and the upper reaches of the St. Clair River are characterized by heavy historical industrial activity, including steel manufacturing and chlor-alkali production.

Key words: Detroit River-Lake St. Clair-St. Clair River corridor, spatial distribution, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, mercury

Introduction

The Detroit River-Lake St. Clair-St. Clair River corridor is a major connecting channel system in the Great Lakes-St. Lawrence Seaway. This waterway is a vitally important binational resource shared by the United States and Canada. Water resources in this binational corridor are heavily used by millions of residents in Michigan and Ontario for recreational boating and angling, navigation, and drinking water. The corridor supports multimillion dollar shipping, manufacturing, mining, and fishing industries.

The corridor has been subjected to loadings of persistent toxics from a variety of sources, including over ten thousand commercial and industrial discharges, sewage treatment plants and combined sewer overflows, and urban runoff (Michigan Department of Environmental Quality 1996). High concentrations of contaminants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs) have been detected both in sediments and biota (Furlong et al. 1988; Kannan et al. 2001; Marvin et al. 2002). Chlorobenzenes, chlorophenols, organochlorines, and a host of heavy metals have also been determined in surface water and fish in the corridor (Kaiser et al. 1985; Gewurtz et al. 2003; Marvin et al. 2004). The Trenton Channel area of the lower Detroit River contains areas of sediment contaminated by PAHs, PCBs, and heavy metals due to historic industrial activities. Kannan et al. (2001), Metcalfe et al. (2000), and Furlong et al. (1988) reported Trenton Channel sediment concentrations of 44,000, 129,700, and 130,000 ng/g, respectively, for PAHs, and concentrations of 25,000, 8,018, and 14,000 ng/g, respectively, for PCBs. Drouillard et al. (2006) published the results of a comprehensive survey of contaminants in Detroit River sediments conducted in 1999; the study found wide-spread contamination of PCBs and PAHs in the Trenton Channel, and the authors concluded that contaminated sediments from the area have the potential to impact environmental quality in western Lake Erie.

The Detroit and St. Clair rivers have been designated as Areas of Concern (AOCs) by the International Joint Commission (Great Lakes Information Network 2009). Currently there are impairments of nine beneficial uses in the corridor (Michigan Department of Environmental Quality 1996), including contamination of fish tissues due to elevated levels of five pollutants (mercury, mirex, chlordane, PCDDs/PCDFs, and PCBs). Most of the advisories (48%) have been issued for PCBs. Between 1993 and 2001, a total of 10 sediment remediation projects were undertaken in the Great Lakes; two were conducted in the Detroit River-western Lake Erie basin. Consequently, the total estimated mass of PCBs removed in the 10 projects was 198 tons (Hartig et al. 2004). However, historically-contaminated sediments continue to be sources of contaminants. The Detroit River watershed is reportedly a dominant source of
contaminants to the western basin of Lake Erie (Oliver and Bourbonniere 1985; Kelly et al. 1991; Carter and Hites 1992). Environment Canada routinely measures the occurrence and spatial distribution of toxic substances in AOCs to further understand the role human activities play in releasing these compounds to the environment, and to provide information on the transport and fate of contaminants in aquatic systems. A program was initiated in 1997 to investigate contaminants associated with suspended sediments in the western Lake Erie-Detroit River-Lake St. Clair-St. Clair River corridor. The goals of this program were to assess the relative importance of sources of contaminants both to the corridor and downstream in western Lake Erie, and to assess the effectiveness of remedial measures to address areas of historically-contaminated sediment. In this paper, we present an overview of the spatial distributions of contaminants including PCBs, PAHs, and mercury in suspended sediments in the corridor over the period of 2000 to 2004.

**Materials and Methods**

**Sample Collection**

Suspended sediment samples accumulated over one-month periods from May to October using single-point sediment trap moorings (Fig. 1) at stations ranging from the outflow of the Detroit River at Lake Erie to southern Lake Huron (Fig. 2 to 4). These sediment trap assemblies were modified from a design previously used for the study of the downflux and composition of particulate matter in the Great Lakes (Charlton et al. 1981; Charlton 1983). The key parameter in the design of the traps is the aspect ratio, defined as the ratio of the internal diameter of the trap tube to the length. The features of this apparatus were described in detail previously (Marvin et al. 2002). The moorings were refurbished monthly, and accumulated material deposited in the traps was removed, transferred to Nalgene containers, and refrigerated. Samples were returned to the laboratory and frozen. Samples collected over the period of 2000 to 2003 were characterized according to particle size and percent total organic carbon (TOC) (Table 1).

**Extraction and Fractionation**

Samples (~5 g) were air-dried and ground with a mortar-pestle, and homogenized. Samples were then spiked with a laboratory surrogate standard containing naphthalene-$d_8$, fluorene-$d_{10}$, pyrene-$d_{10}$, benzo[a]pyrene-$d_{12}$, PCB 30, and PCB 204. Method blanks were carried through the complete sample preparation and analysis procedures.

Samples were extracted using an ASE (accelerated solvent extraction) with dichloromethane followed by an open-column silica gel cleanup procedure. These procedures have been described elsewhere in detail (National Laboratory for Environmental Testing 1997).

<table>
<thead>
<tr>
<th>Station</th>
<th>TOC (%)</th>
<th>Sand (%)</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1167</td>
<td>2.07 ± 0.60</td>
<td>4 ± 2.9</td>
<td>67 ± 1.1</td>
<td>29 ± 4.0</td>
</tr>
<tr>
<td>1175</td>
<td>0.61 ± 0.10</td>
<td>52 ± 5.6</td>
<td>31 ± 6.7</td>
<td>18 ± 3.9</td>
</tr>
<tr>
<td>1172</td>
<td>0.63 ± 0.0</td>
<td>57 ± 1.5</td>
<td>26 ± 2.0</td>
<td>17 ± 0.40</td>
</tr>
<tr>
<td>1165</td>
<td>0.62 ± 0.30</td>
<td>57 ± 3.9</td>
<td>36 ± 9.1</td>
<td>13 ± 1.2</td>
</tr>
<tr>
<td>510</td>
<td>1.13</td>
<td>0</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>1168</td>
<td>1.78 ± 0.70</td>
<td>8 ± 4.2</td>
<td>57 ± 6.2</td>
<td>35 ± 2.5</td>
</tr>
<tr>
<td>1161</td>
<td>1.27 ± 0.80</td>
<td>6 ± 3.9</td>
<td>61 ± 1.6</td>
<td>33 ± 2.9</td>
</tr>
<tr>
<td>1159</td>
<td>1.55 ± 1.1</td>
<td>8 ± 3.1</td>
<td>61 ± 5.7</td>
<td>30 ± 3.0</td>
</tr>
<tr>
<td>1156</td>
<td>0.79 ± 0.50</td>
<td>1 ± 1.0</td>
<td>61 ± 8.3</td>
<td>38 ± 8.2</td>
</tr>
<tr>
<td>1157</td>
<td>1.03 ± 0.60</td>
<td>3 ± 3.9</td>
<td>65 ± 8.1</td>
<td>32 ± 6.8</td>
</tr>
</tbody>
</table>
The column contained anhydrous sodium sulphate and activated silica gel. The column was prewashed with pentane, and then eluted with pentane to collect the PCBs and some low-molecular weight PAHs (Fraction A), followed by elution with of 1:1 (vol/vol) pentane in dichloromethane to collect organochlorines and the remaining PAHs (Fraction B). Fraction volumes were then reduced by rotary evaporation, treated with mercury to remove sulphur, solvent exchanged to isooctane, and transferred to amber vials and refrigerated.

Analyses

The total PAH concentration was determined as the sum of the following 20 individual compounds: naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene, and benzo[g,h,i] perylene. The estimated detection limit for PAHs was 0.06 pg/μL (signal to noise ratio = 3). Spike recoveries, exclusive of naphthalene-d₈, were typically greater than 80%.

PAHs were quantified using a Hewlett-Packard Series II 5890 Gas Chromatograph (GC) (Agilent) with a 30-m HP-5MS column (0.25-mm internal diameter, 0.25-μm film thickness, J&W Scientific), and a Hewlett-Packard 5971A Mass Selective Detector operated in selected ion
monitoring (SIM) mode. GC/MS analyses were performed in the positive ion electron impact mode (EI+) with helium as the carrier gas at a flow rate of 1.0 mL/min. Samples were injected using an on-column injector. The temperature program was as follows: initial temperature 70°C; 70 to 160°C at 10°C/min; 160 to 300°C at 5°C/min; hold for 15 min. The instrument equilibration time was 3 min. The GC column performance was monitored every 4 to 5 samples using a calibration solution containing PAHs at concentrations of roughly 1 ng/μL.

PCBs were analyzed using a Hewlett-Packard Series II 5890 GC equipped with dual electron capture detectors, hydrogen as the carrier gas at a flow rate of 1.0 mL/min, splitless injection, and dual columns (30 m, 0.25-mm internal diameter, 0.25-μm stationary phase DB-5MS; and 30 m, 0.25-mm internal diameter, 0.25-μm stationary phase DB-1, J&W Scientific). The temperature program was as follows: initial temperature 70°C, 70 to 150°C at 15°C/min; 150 to 270°C at 2°C/min; 270 to 300°C at 20°C/min; hold for 5 min. Instrument equilibration time was 3 min. Instrument calibration was performed using five levels of a mixed 132-congener PCB standard (4 to 6 pg/μL, 40 to 60 pg/μL, 80 to 120 pg/μL, 200 to 300 pg/μL, and 400 to 600 pg/μL). Method blanks and standard reference materials were processed with each set of 10 field samples.

Fig. 3. Spatial distribution of total PAH concentrations (ng/g dry weight) in Detroit River-Lake St. Clair-St. Clair River corridor suspended sediments in July 2000 and July 2004.
Total mercury was determined by digestion with hot nitric acid and hydrochloric acid followed by cold vapour atomic absorption spectrometry according to standard United States Environmental Protection Agency methods (United States Environmental Protection Agency 1981).

Samples for particle size analysis were weighed (5 to 8 g) and mixed with sodium metaphosphate for 15 minutes. Sand/gravel content was calculated by passing sediments through a nest of sieves from 3.5-mm down to 0.063-mm openings. Silt/clay ranging from 0.063 mm down to 0.00024 mm was analyzed by a sedigraph analyzer. TOC was calculated by summing percentages of organic carbon and inorganic carbon. Analyses were performed using a two-temperature dry combustion method. Sediments were dried in the oven for a minimum of 2 hours and then weighed to 0.5000 g for both organic and inorganic carbon content analyses. Organic carbon was analyzed by burning samples at 500°C for 250 seconds and then recording the percentage of carbon. Inorganic carbon was analyzed using the same sample
by burning at 1,370°C for 60 seconds and recording the percentage of carbon.

Results and Discussion

Suspended Sediment Characterization

Particle size distributions and percent TOC of suspended sediments in the corridor generally remained consistent over the period of the study (Table 1). Data presented for different contaminant classes represent different sampling intervals; for PCBs and PAHs, data for 2000 and 2004 represent a single monthly sampling interval (July). July samples were selected due to the propensity for severe summer storms to result in considerable runoff from the watershed and significant resuspension and transport downstream of contaminated sediments. Data presented for mercury correspond to annual means resulting from analysis of all samples collected over the period of 2002 to 2004. Therefore, mercury is the only contaminant class presented in this study for which any statistical analysis of interseasonal or interannual trends can be presented.

Spatial Distribution of PCBs

Previous studies of Detroit River sediments reported PCB concentrations ranging from 33 to 14,000 ng/g (Kaiser et al. 1985; Furlong et al. 1988; Marvin et al. 2002). PCBs were found in all suspended sediment samples with concentrations in 2004 ranging from 21 to 1,200 ng/g (dry weight), and from 10 to 2,800 ng/g in 2000. Tables 2 and 3 show homologue (sum of Cl2 to Cl10 homologues) and total PCB concentrations in the Detroit River-Lake St. Clair-St. Clair River corridor in July 2004 and July 2000, respectively. Spatial distributions of PCBs in corridor suspended sediments were similar among the two years (Fig. 2). Sum PCB concentrations increased (8- to 20-fold) from upstream to downstream locations along the U.S. side of the Detroit River in both 2000 and 2004. A similar, but less substantial (3-fold), trend was observed along the Canadian side of the river. These results were similar to the findings of Drouillard et al. (2006) and indicated the presence of multiple inputs of PCBs on the U.S. side of the river.

The highest concentrations of PCBs throughout the entire corridor in both 2000 and 2004 were associated with stations in the Trenton Channel in the lower reaches of the Detroit River; this area is characterized by large areas of sediment severely contaminated as a result of historical industrial activities. It has been reported that the Trenton Channel contains the greatest volume of contaminated sediment within the Detroit River-Lake St. Clair-St. Clair River corridor (Michigan Department of Environmental Quality 1996). The highest concentrations of PCBs were observed at station 1161 in both 2000 and 2004; this station is located in the upper Trenton Channel near the mouth of Monguagon Creek, an area of intensive historical industrial activity (Fig. 2). Another station further downstream in the lower Trenton Channel (station 1159) also exhibited relatively high PCB concentrations.

Station 1169 was sampled in 2000 and exhibited a total annual mean PCB concentration of 675 ng/g dry weight (range of 180 to 1,125 ng/g over a seven-month period). This station was located downstream of Connors Creek, which was identified as a potential source of PCBs to the upper Detroit River (Kannan et al. 2001). During 2003 to 2004, contaminated sediments in Connors Creek were removed during remediation activities; it was estimated that 302 kg of PCBs were removed from Connors Creek (Hartig et al. 2004). Follow-up sampling of this area is ongoing.

The PCB concentrations at station 1168 near the mouth of the Rouge River were roughly 10- to 15-fold lower than at station 1161 (Tables 2 and 3). The Rouge River is one of the major tributaries draining from the U.S. shoreline into the Detroit River, and more than 50% of the land use in the basin is residential, commercial, and industrial (Michigan Department of Environmental Quality 1996). It has been reported that PCBs, PAHs, PCDDs/PCDFs, PCNs, and other organic compounds are prevalent in sediments of the Rouge River basin (Hamdy and Post 1985; Kannan et al. 2001). The typically lower PCB concentrations at upstream sites, compared with sites in the Trenton Channel, indicate that a substantial portion of the total PCB loading to the western basin of Lake Erie.

<table>
<thead>
<tr>
<th>Homologue</th>
<th>Stations (2004)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>510</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>8.0</td>
</tr>
<tr>
<td>5</td>
<td>7.8</td>
</tr>
<tr>
<td>6</td>
<td>9.8</td>
</tr>
<tr>
<td>7</td>
<td>0.4</td>
</tr>
<tr>
<td>8</td>
<td>2.0</td>
</tr>
<tr>
<td>9</td>
<td>0.32</td>
</tr>
<tr>
<td>TOTAL PCBs</td>
<td>33</td>
</tr>
</tbody>
</table>
Contaminants in the Detroit River Corridor

is the result of legacy sources associated primarily with historical industrial activities in the lower reaches of the Detroit River. These results are corroborated by those of Drouillard et al. (2006); although multiple sources of PAHs and PCBs were detected in the upper and middle reaches of the River along the U.S. shoreline, the greatest degree of sediment contamination was found within the Trenton Channel.

The influence of contaminated sediments in the Trenton Channel as a source of PCBs to western Lake Erie was also evidenced through the comparison of stations 1157 and 1156, which are located at the same latitude, but on opposite sides at the mouth of the Detroit River (Fig. 2). Station 1157 is influenced primarily by flow emanating from the Trenton Channel, while station 1156 is influenced primarily by the water flowing east of Grosse Ile. Drouillard et al. (2006) reported that high flow rates within the shipping channels segregate material originating from either side of the river. The PCB concentrations in both 2000 and 2004 were roughly two-fold higher at station 1157 compared with station 1156.

The PCB levels at sites in the upper reaches of the St. Clair River (stations 1165, 1172, and 1175) and in Lake St. Clair (station 510) were relatively low in comparison with the PCB levels measured in the Trenton Channel (Tables 2 and 3). The southern Lake Huron station exhibited the lowest concentrations of PCBs (15 to 20 ng/g). These relatively low PCB levels are typical of PCB concentrations in bottom sediments of southern Lake Huron, and provide an upstream reference value against which the downstream connecting channels can be assessed. These data indicate that industrial areas in the upper reaches of the St. Clair River do not represent substantial sources of PCBs to the corridor.

Spatial Distribution of PAHs

PAHs were detected in all suspended sediment samples analyzed; total PAH concentrations in the Detroit River-Lake St. Clair-St. Clair River corridor ranged from 640 to 52,000 ng/g dry weight in 2004, and from 240 to 82,000 ng/g dry weight in 2000 (Tables 4 and 5, Fig. 3). Sources of PAHs are primarily related to the combustion of fossil fuels and are predominant in areas of intense industrial activities. The spatial distributions shown in Fig. 3 reflect the urban and industrial land use patterns in the corridor (Michigan Department of Environmental Quality 1996). The total PAH concentrations measured in this study were within the range of those reported for bottom sediments collected in 1988 from the Trenton Channel (350 to 130,000 ng/g dry weight) (Furlong et al. 1988), and from the Detroit River (394 to 43,800 ng/g dry weight) (Kannan et al. 2001).

The comparison of PAH concentrations in 2004 at all ten study sites yielded a spatial pattern similar to that observed in 2000 (Fig. 3). The highest PAH concentrations were found in the Trenton Channel area.
TABLE 4. PAH concentrations (ng/g dry weight) in Detroit River-Lake St. Clair-St. Clair River corridor suspended sediments collected in July 2004

<table>
<thead>
<tr>
<th></th>
<th>Stations (2004)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S10$</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>220</td>
</tr>
<tr>
<td>Anthracene</td>
<td>6</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>94</td>
</tr>
<tr>
<td>Pyrene</td>
<td>96</td>
</tr>
<tr>
<td>Benzo[a]antracene</td>
<td>21</td>
</tr>
<tr>
<td>Chrysene</td>
<td>59</td>
</tr>
<tr>
<td>Benzo[b]fl + benzo[k]fl.</td>
<td>193</td>
</tr>
<tr>
<td>Benzo[e]pyrene</td>
<td>93</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>65</td>
</tr>
<tr>
<td>Perylene</td>
<td>64</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>60</td>
</tr>
<tr>
<td>Dibenzo[a,h]antracene</td>
<td>18</td>
</tr>
<tr>
<td>Benzo[ghi]perylen</td>
<td>106</td>
</tr>
<tr>
<td>phenanthrene/antracene</td>
<td>37</td>
</tr>
<tr>
<td>Benzo[e]pyrene/Benzo[a]pyrene</td>
<td>1</td>
</tr>
</tbody>
</table>

Total PAH (ng/g)  
1,100  4,300  9,100  52,000  38,000  850  640  38,000  1,200  1,100

*Benzo[b]fluoranthene + benzo[k]fluoranthene.
*bBenzo[e]pyrene/Benzo[a]pyrene.

of the lower Detroit River (stations 1159, 1161) and near the mouth of the Rouge River (station 1168, Fig. 3); PAH concentrations at these sites ranged from 38,000 to 82,000 ng/g. Comparison of PAH concentrations at the two stations at the outflow of the Detroit River to western Lake Erie (1156 and 1157) yielded results similar to those of PCBs in that concentrations were substantially higher on the west side of the river; PAH concentrations at station 1157 were roughly two- to four-fold higher than concentrations at station 1156 (Tables 4 and 5). The spatial distributions of PAHs and PCBs in the corridor were generally similar, except for station 1168. While PCB concentrations at this station were substantially lower than the downstream locations, PAH concentrations were typically similar to or higher than those of the Trenton Channel stations. Kannan et al. (2001) previously identified the Rouge River as a major source of PAHs to the Detroit River. More than 50% of land use in the Rouge River watershed is residential, commercial, or industrial. We attributed our observations to the fact that PAHs continue to be produced by a myriad of combustion sources, and are typically prevalent in sediments in proximity to highly industrialized areas. The magnitude of contamination at stations 1168, 1161, and 1159 indicate an additional contribution from resuspended PAH-contaminated bottom sediments in these areas; there are no apparent land-based activities or sources in this area that could account for the observed increased PAH contamination. However, this possibility cannot be entirely discounted.

The PAH concentrations in the upper reaches of the St. Clair River (stations 1165, 1172, and 1175) and in Lake St. Clair (station 510) were typically elevated, compared with the southern Lake Huron station (station 1167, Tables 4 and 5); total PAH concentrations in 2004 in the St. Clair River and Lake St. Clair were roughly two-fold higher compared with the southern Lake Huron station (Table 4). However, in 2000 total PAH concentrations were more similar among all of the Lake St. Clair, St. Clair River, and southern Lake Huron stations (Table 5). The upper reaches of the St. Clair River on the Canadian side are characterized by intensive urbanization and industrialization, including the presence of coal-fired power generating plants.

Comparison of PAH profiles among these sites was conducted to provide further information on local and/or regional sources. The ratios of phenanthrene/antracene and benzo[e]pyrene/benzo[a]pyrene were roughly 4.5 and 1.5, respectively, in Lake Huron suspended sediments, and reflected the relative short half-life for the photolysis of anthracene and benzo[a]pyrene (Behymer and Hites 1985). We hypothesize that suspended sediments collected at the southern Lake Huron site would contain absorbed PAHs subjected to greater exposure to sunlight, compared with urbanized areas of the corridor such as the Detroit River, where the ratios of phenanthrene/antracene and benzo[e]pyrene/benzo[a]pyrene were roughly 3.0 and 0.7. These results were similar to those reported by Furlong et al. (1988) for Trenton Channel sediment samples. Water quality data, including Secchi depth, conductivity, and turbidity (unpublished data), all indicate substantially greater water clarity, and presumably greater exposure to ultraviolet light in the water column, at the southern Lake Huron station compared with the stations in the rivers.
Contaminants in the Detroit River Corridor

Spatial Distribution of Mercury

Mercury data presented are the annual mean concentrations corresponding to a total of 60 samples collected in the Detroit River-Lake St. Clair-St. Clair River corridor over the period of 2002 to 2004 (Table 6, Fig. 4). Mercury concentrations were elevated throughout the corridor, with annual means at stations 1159 and 1161 exceeding the Canadian probable effect level (PEL, 0.486 mg/kg; CCME 1999) for bottom sediments in 2002, and at station 1175 in 2003. In contrast to the results for PCBs and PAHs, the spatial distributions of mercury were more consistent throughout the corridor over the period of 2002 to 2004 (Fig. 4).

The prevalence of mercury in suspended sediments throughout the corridor is reportedly due to historical contamination arising primarily from chlor-alkali production both in the lower reaches of the Detroit River and upper reaches of the St. Clair River (Walters et al. 1972, 1974; Kovacik and Walters 1973; Thomas and Jaquet 1976; Marvin et al. 2004). Historic mercury cell plants located in Sarnia, Ontario and operated since 1949 in the upper reaches of the St. Clair River reportedly discharged up to 90 kg per day of mercury to the river during their periods of operation (Toms 1999), resulting in areas of severely-contaminated sediments adjacent to the shoreline (OWRC 1970; Wolery and Walters 1974; Johnson and Kauss 1989). In 1970, treatment facilities were installed to eliminate mercury discharges to the river; these plants were voluntarily decommissioned shortly thereafter. However, three highly-impacted sediment zones remained and continued to act as in-place sources of contamination (St. Clair River Remedial Action Plan 2001). Dow Canada completed a clean up of approximately 200 m$^3$ of sediment in this area in 1996, and initiated further sediment remediation activities in 2002 that ultimately resulted in the removal of approximately 13,370 m$^3$ of bottom sediment (Lake St. Clair Canadian Watershed Coordination Council 2005). Since target reductions in discharges of mercury continue to be met (90% reduction in releases in the Great Lakes basin between 1988 and 2006, GLBTS 2009), we presume that in-place contaminated sediments in the St. Clair River are responsible for the observed mercury distribution rather than shoreline-based inputs.

The presence of upstream sources of mercury is evidenced through comparison of stations 1156 and 1157 at the mouth of the Detroit River; while PCB and PAH data exhibited an apparent gradient toward increasing concentrations across the river from east to west, mercury concentrations were indistinguishable between these two stations (Fig. 4, Table 6). Drouillard et al. (2006) presented a similar argument for octachlorostyrene in that the lack of cross-river gradients in concentrations in the Detroit River was indicative of the prevalence of sources upstream. We would expect a cross-river gradient at stations 1156 and 1157 approximating those for PAHs and PCBs if more local sources associated with urbanization/industrialization were the major contributors to mercury loadings.
Mercury concentrations in the corridor were also calculated normalized to TOC (Table 6). In considering the physical characteristics of the suspended sediments (Table 1), it was evident that trapped material accumulated at stations in the upper reaches of the St. Clair River (stations 1175, 1172, and 1165) was of a coarser nature; suspended sediments from these stations were greater than 50% sand, with correspondingly low TOC concentrations. When normalized to TOC, mercury concentrations at the upper St. Clair River stations were generally higher than stations in the lower reaches of the Detroit River. The highest TOC-normalized mercury concentrations throughout the entire corridor were observed at stations 1165 (75 mg/kg TOC) and 1172 (64.3 mg/kg TOC) (Table 6). In addition, TOC-normalized mercury concentrations in the upper St. Clair River were roughly 15- to 25-fold higher than the upstream station in southern Lake Huron.

Mercury contamination in bottom sediments at Station 510 in the central area of Lake St. Clair (0.434 mg/kg) (Gewurtz et al. 2007), as measured during a lake-wide survey conducted in 2000, was within the range of the annual mean concentrations (0.281 to 0.460 mg/kg) for suspended sediments reported in this study. Similarly, the mean mercury concentration of bottom sediments in the western basin of Lake Erie (0.402 mg/kg) was within the range of annual means for suspended sediments in the Detroit River (0.264 to 0.514 mg/kg, Table 6). In both cases, mercury in sediments of open-lake areas of lakes Erie and St. Clair represents significant enrichment due to anthropogenic activities; accumulation of these sediments in our sediment traps provide evidence that contaminated sediments in the Detroit and St. Clair rivers are mobile and continue to migrate and potentially impact downstream areas. However, it should also be noted that the most recent bottom sediment data for both lakes St. Clair and Erie show dramatic declines in mercury contamination of the past 30 years; the estimated reduction in mercury sediment contamination in western Lake Erie has been estimated to be 60% (Marvin et al. 2004).

Concentrations of mercury throughout the corridor were consistently above the Canadian threshold effect level (TEL) guideline (0.170 mg/kg; CCME 1999), except in southern Lake Huron where concentrations were consistently relatively low. Exceedances of the Canadian PEL (0.486 mg/kg) are shown in bold typeface in Table 6; this guideline was exceeded at stations 1159 and 1161 in the lower reaches of the Detroit River in the Trenton Channel in 2002. The TEL represents the concentration below which adverse biological effects are expected to occur rarely, while the PEL defines a level above which adverse effects are expected to occur frequently (CCME 1999). Although these guidelines should only be used as a screening tool as opposed to a risk assessment tool, the guideline exceedances in the Trenton Channel area suggest these suspended sediments have the potential to illicit adverse biological effects. The range of annual average mercury concentrations in suspended sediments at the Lake Huron station (0.058 to 0.063 mg/kg, Table 6) was only slightly higher than the lake-wide average bottom sediment concentration (0.043 mg/kg) (Marvin et al. 2004). Mudroch et al. (1988) estimated the background concentrations in bottom sediments of the depositional basins of Lake Huron to be in the range of 0.040 to 0.080 mg/kg. Therefore, Lake Huron does not appear to represent a significant source of mercury to the corridor.

Conclusions

Spatial distributions of all contaminants in suspended sediments showed little variation over the course of the study. The highest concentrations of PCBs in the Detroit River–Lake St. Clair–St. Clair River corridor in both 2000 and 2004 were associated with stations in the Trenton Channel in the lower reaches of the Detroit River. Assessment of the spatial pattern in PCB contamination indicated that a large portion of PCB loadings to the western basin of Lake Erie are associated with historical industrial activity in the Trenton Channel. The spatial distributions of PAHs and PCBs in the corridor were generally similar; however, data from a station at the mouth of the Rouge River in the middle reaches of the Detroit River suggested contributions from both

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**Table 6. Annual mean concentrations of mercury in Detroit River-Lake St. Clair-St. Clair River corridor suspended sediments collected over 2002 to 2004**

<table>
<thead>
<tr>
<th>Stations</th>
<th>2002</th>
<th>2003</th>
<th>2004</th>
<th>2002</th>
<th>2003</th>
<th>2004</th>
</tr>
</thead>
<tbody>
<tr>
<td>1167</td>
<td>0.060 ± 0.01</td>
<td>0.058 ± 0.02</td>
<td>0.063 ± 0.02</td>
<td>2.90</td>
<td>2.80</td>
<td>3.04</td>
</tr>
<tr>
<td>1175</td>
<td>0.289 ± 0.19</td>
<td>0.259 ± 0.22</td>
<td>0.182 ± 0.14</td>
<td>47.4</td>
<td>42.5</td>
<td>29.8</td>
</tr>
<tr>
<td>1172</td>
<td>0.287 ± 0.16</td>
<td>0.287 ± 0.21</td>
<td>0.405 ± 0.16</td>
<td>45.6</td>
<td>45.6</td>
<td>64.3</td>
</tr>
<tr>
<td>1165</td>
<td>0.465 ± 0.20</td>
<td>0.345 ± 0.08</td>
<td>0.322 ± 0.07</td>
<td>75.0</td>
<td>55.6</td>
<td>51.9</td>
</tr>
<tr>
<td>510</td>
<td>0.460 ± 0.29</td>
<td>0.327 ± 0.12</td>
<td>0.281 ± 0.08</td>
<td>40.7</td>
<td>28.9</td>
<td>24.9</td>
</tr>
<tr>
<td>1168</td>
<td>0.265 ± 0.07</td>
<td>0.322 ± 0.12</td>
<td>0.307 ± 0.09</td>
<td>14.9</td>
<td>18.1</td>
<td>17.2</td>
</tr>
<tr>
<td>1161</td>
<td>0.514 ± 0.27 *</td>
<td>0.391 ± 0.11</td>
<td>0.456 ± 0.07</td>
<td>40.5</td>
<td>30.8</td>
<td>35.9</td>
</tr>
<tr>
<td>1159</td>
<td>0.491 ± 0.14 *</td>
<td>0.343 ± 0.09</td>
<td>0.478 ± 0.10</td>
<td>31.7</td>
<td>22.1</td>
<td>30.8</td>
</tr>
<tr>
<td>1156</td>
<td>0.438 ± 0.06</td>
<td>0.290 ± 0.03</td>
<td>0.325 ± 0.03</td>
<td>55.4</td>
<td>36.7</td>
<td>41.3</td>
</tr>
<tr>
<td>1157</td>
<td>0.444 ± 0.05</td>
<td>0.264 ± 0.02</td>
<td>0.274 ± 0.02</td>
<td>43.1</td>
<td>25.6</td>
<td>26.6</td>
</tr>
</tbody>
</table>

* Asterisk (*) denotes an exceedance of the Canadian guideline value of 0.486 mg/kg (CCME 1999).
contemporary industrial emissions and contaminated sediments associated with historical industrial activities.

In contrast to the results for PCBs and PAHs, the spatial distributions of mercury were more consistent throughout the entire length of the corridor. This consistency was attributed to the presence of sources to both the Detroit and St. Clair rivers, and more specifically historical bottom sediment contamination associated with chlor-alkali production. This same rationale, i.e., a lack of upstream/downstream gradients, was used by Drouillard et al. (2006) in concluding that octachlorostyrene in Detroit River bottom sediments is derived primarily from upstream sources in the St. Clair River. In the case of all contaminants, the comparison of concentrations at two stations (1156 and 1157) located at the mouth of the Detroit River assisted in the identification of primary source areas. While PCB and PAH data exhibited a definitive gradient toward increasing concentrations from east to west, and thereby implicating the lower and middle reaches of the Detroit River as source areas, mercury concentrations were indistinguishable between these two stations. In the case of mercury, sediments of open-lake areas of lakes Erie and St. Clair exhibited significant enrichment due to anthropogenic activities, which indicated that contaminated sediments originating in the Detroit and St. Clair rivers are mobile and able to impact downstream areas. Other groups have reported that contaminated sediments in the lower reaches of the Detroit River can influence contaminant loadings to Lake Erie, particularly during periods of certain meteorological conditions (Drouillard et al. 2006).

The results of the aforementioned studies show that the focus of the binational agencies on the St. Clair and Detroit rivers through the respective Remedial Action Plans (RAPs), and the associated expenditures on sediment remediation activities ($130 million USD over the past decade [Heidtke et al. 2006]), have been well justified. The assessment of temporal trends in environmental compartments of the Detroit River over the period of the 1970s to the mid-1990s revealed dramatic reductions in levels of PCBs (Heidtke et al. 2006). However, our current study, and those collectively reported by Heidtke et al. (2006) for PCBs, show less definitive improvement since the mid-1990s. It should be acknowledged that considerable additional sediment remediation activities were undertaken in both the lower reaches of the Detroit River and upper reaches of the St. Clair River over the period during which our study was being conducted; future suspended sediment data from our sediment trap studies may reflect additional reductions in sediment contamination.

Acknowledgments

We thank the Captain and crew of the CCGS Limnos and Environment Canada Technical Operations Burlington for technical support.

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Received: 9 March 2009; accepted: 12 January 2010.
Caractérisation et traitement physico-chimique des lixiviats de la décharge publique d’El-Kerma (Algérie) par adsorption en continu sur de la sciure de bois naturelle et activée chimiquement

Characterization and physico-chemical treatment of El-Kerma (Algeria) landfill leachates by batch adsorption on untreated and chemically activated sawdust

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La décharge publique d’El-Kerma d’Oran (Ouest algérien) constitue un exemple type de détérioration des ressources naturelles en eau par les déchets solides. Elle génère des volumes importants de lixiviats à forte charge polluante (CE extrême de 130 mS/cm et COD extrême de 28000 mg O2/L), dont le traitement s'impose. Le traitement physico-chimique des lixiviats de cette décharge par adsorption en continu de la matière organique sur de la sciure de bois activée à la soude 3 N (SB3), de masse optimale de 0,3 g, à un temps d'équilibre de 40 min, à pH 11,0 et à une température de 55°C, a donné une capacité maximale d'adsorption de 100 mg/g, selon le modèle de Langmuir. Cette adsorption est endothermique et s'effectue à une cinétique rapide et du premier ordre. Les essais de traitement successif des lixiviats bruts effectués sur une série de cinq réacteurs ont permis de réaliser un taux d'abattement de la matière organique de 98 % sur la sciure SB3 et dès à la sortie du troisième réacteur. Le matériau adsorbant utilisé a montré une efficacité comparable à celle d'autres matériaux largement utilisés dans l'épuration des effluents.

Mots clés : caractérisation; lixiviats de décharge; adsorption; sciure de bois; COD

Introduction

Actuellement, l’augmentation de la production des déchets solides va de pair avec l’essor démographique et l’intensification des activités socio-économiques. Dans les pays en voie de développement, et particulièrement en Algérie, le mode de gestion des déchets solides le plus adopté correspond à la mise en décharge. Il s'agit principalement de décharges non contrôlées et à ciel ouvert, où tous les types de déchets sont rejetés à l’état brut et mélangés : urbains, industriels, hospitaliers et agricoles (AND 2003; MATE 2003). La mise en opération de ces sites de décharge « sauvage » n’a été précédée par aucune étude d’impact sur l’environnement.

De manière générale, ces décharges sont à l’origine de nuisances multiples et fréquentes : odeurs fétides, rongeurs, chiens enragés, autoincinération et fumées asphyxiantes, insectes et vecteurs de maladies, poussières et objets volants, biogaz et lixiviats. En effet, de tels lixiviats sont...
générés à des volumes importants et à une forte charge polluante, de nature organique et inorganique. Leur rejet à l’état brut et sans aucun traitement préalable engendrer les impacts environnementaux suivants : pollution des sols, contamination des eaux souterraines et de surface, atteinte à la santé humaine, etc. (AND 2003; DEO 2003; MATE 2003).

Un exemple type est celui de la décharge publique d’El-Kerma de la ville d’Oran (Ouest algérien) qui a été créée en 1986 et qui s’étend sur une superficie de plus de 4 km². Elle se situe à 15 km au sud d’Oran et reçoit quotidiennement de tout le groupement urbain d’Oran environ 1 200 tonnes de déchets solides à l’état brut et mélangés, constitués majoritairement de matières fermentescibles (plus de 70 % en poids humide) (EPIC Propreté d’Oran 2007).

Cette décharge non contrôlée et mal exploitée est à l’origine d’un lixiviat qui n’est pas drainé et qui risque, après accumulation, de s’infiltrer dans le sous-sol et de contaminer la nappe phréatique qui s’écoule en cette zone à environ 20 mètres de profondeur. À cet effet, le traitement des lixiviats de la décharge d’El-Kerma s'impose.

Dans ce cadre, les objectifs suivants ont été fixés pour le présent travail : d’une part, de déterminer les aspects quantitatifs et qualitatifs des lixiviats de la décharge d’El-Kerma, indispensables pour caractériser la charge polluante et d’estimer les risques que présentent ces lixiviats sur la qualité des eaux de la nappe phréatique ; d’autre part, de proposer et d’étudier un procédé de traitement de ces lixiviats, peu coûteux et efficace. Le procédé recherché vise à obtenir un abattement très significatif de la charge organique du lixiviat et pourrait ainsi être transposé à d’autres sites de décharge actuels et futurs.

Notre contribution va donc consister à un traitement physico-chimique par adsorption en continu de la matière organique sur un matériau naturel, soit de la sciure de bois, naturelle et activée chimiquement. Cette matière organique sur un matériau naturel, soit de la sciure de bois lavée à l’eau distillée, filtrée sur Büchner et séchée à 100°C. Après filtration sur Büchner, la sciure ainsi récupérée est transportée immédiatement au laboratoire où ils ont été placés dans un réfrigérateur, à 4°C et à l’obscurité. Les échantillons de lixiviats destinés à des analyses de cations et d’ions métalliques sont acidifiés, dès le prélèvement, à l’acide nitrique concentré, à raison de 5 mL/L.

Tous les paramètres chimiques des lixiviats ont été déterminés selon les méthodes standards pour l’analyse des eaux usées (Rodier 1984; APHA, AWWA, WPCF 1995). La teneur de matières en suspension (MES) a été déterminée par la méthode de filtration. La Demande Chimique en Oxygène (DCO) est analysée à l’aide d’un DCO-mètre type thermoréacteur CR 2010 et la Demande Biologique en oxygène (DBO₅) est mesurée à l’aide d’un DBO₅-mètre Model BSF-Méfgerat 1002. Les phénols, nitrites, nitrates, phosphates et sulfates ont été déterminés avec un spectrophotomètre dans le visible type Perkin Elmer Lambda 20. Le Carbone Organique Total (COT) est analysé grâce à un COT-mètre type Elemental Analyser High TOC II. Les hydrocarbures totaux sont extraits avec le tétrachlorure de carbone et dosés par spectrométrie d’absorption infrarouge type SP3 200 IFR-RED. Le potassium et le sodium ont été analysés par spectrophotométrie à flamme type Jenway PST7. Le calcium et le magnésium ont été dosés par complexométrie avec l’EDTA et les éléments métalliques (Fe, Pb, Cu, Zn, Mn, Cd, Ni, Cr) ont été analysés par absorption atomique type PYE-UNICAM SP9.

Préparation de la sciure de bois

La sciure de bois est le matériau naturel utilisé dans l’adsorption de la charge organique, exprimée en DCO, des lixiviats de la décharge publique d’El-Kerma. Celle-ci provient d’un pin d’origine caucasienne, préalablement tamisée sur tamiseur de type ENDECOTTS model EVL1, et seule la fraction inférieure à 1 mm a été retenue. Pour les essais d’adsorption, la sciure de bois a été utilisée sous quatre formes distinctes : SB, sciure de bois naturelle lavée à l’eau distillée, filtrée sur Büchner et séchée à l’étuve à 100°C jusqu’à l’obtention d’une poudre ; SB1, SB2 et SB3, sciure de bois traitée à la soude à différentes normalités, soit 1 N, 2 N et 3 N, respectivement. Pour les trois sciures de bois traitées, une quantité de 100 g de sciure naturelle est dispersée dans 500 mL de solution de soude à la normalité désirée. Le mélange est maintenu ensuite sous agitation magnétique modérée, à température ambiante (25°C), pendant 1 heure et laissé reposer durant 24 heures. Ensuite, ce mélange est lavé à l’eau distillée jusqu’à un pH proche de la neutralité. Après filtration sur Büchner, la sciure ainsi récupérée est séchée à 100°C.

Essai d’abattement en statique de la DCO des lixiviats par adsorption

Vérification de la stabilité de la DCO initiale des lixiviats bruts. À cause de la variation temporelle des teneurs de la matière organique, nous avons procédé à une vérification de la concentration initiale de la DCO du lixiviat brut à traiter, avant chaque essai expérimental. La DCO initiale, retenue dans tous nos essais, est égale à...
28000 mg d'O₂/L, valeur considérée comme extrême. Ce lixiviat a été prélevé au niveau de la décharge publique d'El-Kerma, en février 2007.

**Optimisation des paramètres d'adsorption.** Tous les essais d'adsorption se sont déroulés dans un réacteur statique, à température ambiante (25°C) et avec des lixiviats bruts à pH 8,4. En raison de leur caractère très encrassant, ces lixiviats ont été filtrés pour l'élimination des matières en suspension affectant la lecture de la DCO et ensuite dilués à 1%. À chaque mesure de la DCO, un essai à blanc servant comme témoin (sciure de bois + eau distillée) a été réalisé en parallèle, afin de pouvoir calculer la DCO à l'équilibre.

Pour chaque forme du biomatériaux (SB, SB1, SB2 et SB3), nous avons procédé à l'optimisation des facteurs déterminants du processus d'adsorption, à savoir la masse d'adsorbant, le temps de contact et le pH du milieu. L'optimisation de la masse a consisté à la faire varier à des pas de 0,05 g, mélangé à chaque fois avec 50 ml du lixiviat préalablement filtré et dilué. Le mélange obtenu est soumis à une agitation magnétique pendant 2 heures. Ensuite, la suspension est filtrée et la lecture de la DCO résiduelle est effectuée. Le pourcentage d'adsorption (ou taux d'élimination) de la DCO est calculé à l'aide de l'équation suivante :

\[
\% \text{ d'adsorption} = \left[\frac{(\text{DCO}_i - \text{DCO}_e)}{\text{DCO}_i}\right] \times 100 \quad (1)
\]

où DCO₀ et DCOₑ désignent respectivement la DCO initiale et résiduelle (mg d'O₂/L).

Pour chaque masse optimale obtenue des quatre formes du biomatériaux, nous avons procédé aussi varier le temps de contact à des pas de 5 à 10, jusqu'à l'obtention du palier de saturation de la sciure. Aussi, afin d'évaluer l'influence du pH du lixiviat sur l'adsorption de la DCO par la sciure de bois, nous avons mené une série d'essais à différents pH (3,0 à 11,0), pour les valeurs optimales de la masse et du temps de contact obtenues. Le mélange considéré dans chaque manipulation est maintenu à 50 ml du lixiviat filtré et dilué et a subi le même protocole décrit précédemment (agitation, filtration et lecture de la DCO résiduelle).

**Détermination des isothermes d'adsorption.** Dans les conditions optimales précédentes, nous avons établi des isothermes d'adsorption à des températures différentes (25, 35, 45 et 55°C). Pour chaque température, nous avons procédé à une variation de la DCO initiale, à des pas de 50 mg d'O₂/L, sur une gamme de 50 à 900 mg d'O₂/L, par dilution. Le mélange est toujours de 50 ml du lixiviat, filtré et dilué et a subi le même protocole décrit précédemment (agitation, filtration et lecture de la DCO résiduelle).

La quantité de matière organique polluante adsorbée est calculée d'après l'équation suivante :

\[
Q_e = \frac{x}{m} = \left[\frac{(\text{DCO}_i - \text{DCO}_e)}{m}\right] \times V \quad (2)
\]

où \(Q_e\) : quantité de matière organique fixée par unité de masse de sciure, ou capacité d'adsorption (mg/g); \(m\) : masse optimale de sciure de bois (g); et \(V\) : Volume du mélange fixé à 50 mL.

**Résultats et discussion**

**Caractérisation physico-chimique des lixiviats**

La composition chimique des lixiviats est spécifique à chaque décharge. En effet, elle varie étroitement avec la nature et l'âge de la décharge, le type de déchets et leur degré de décomposition, la méthode de mise en décharge, la nature du site d'enfouissement et les conditions climatiques (Navarro et al. 1988; Matejka et al. 1994; Khattabi 2002; Aluko et al. 2003; Chofqi et al. 2004; Kurniawan et al. 2006; Renou et al. 2008).

Les lixiviats de la décharge d'El-Kerma d'Oran sont de couleur noirâtre et d’odeur fécaloïde. L'examen des valeurs moyennes des paramètres physico-chimiques, calculées sur les trois années 2005, 2006 et 2007 et qui sont rassemblées dans le Tableau 1, montre que le lixiviat étudié accuse une charge polluante diversifi ée et élevée. En effet, la conductivité électrique moyenne est de l'ordre de 120,3 mS/cm, indiquant la forte minéralisation des lixiviats de la décharge d’El-Kerma. Cette minéralisation est principalement attribuable aux paramètres suivants : chlorures (3379 mg/L), sulfates (1717 mg/L), ammonium (2726 mg/L) et sodium (1840 mg/L). Les valeurs moyennes des paramètres pH, MES et turbidité sont respectivement de 8,19, 1149 mg/L et 732 NTU. Ceci montre, d’une part, le caractère basse des lixiviats de la décharge étudiée et d’autre part, leur forte charge minérale et organique (Aluko et al. 2003).

En ce qui concerne la charge organique, les teneurs moyennes de la DCO et de la DBO₅ sont respectivement de 19333 et 3301 mg d’O₂/L, avec un rapport DBO₅/DCO de 0,17. Ceci dénote que le lixiviat et la décharge étudiées sont en phase intermédiaire, voire à sa fin (Chian 1977; Amokrane 1994; Vilomet 2000; Hakou et al. 2001; Khattabi 2002; Chofqi 2004; Kurniawan et al. 2006).

L'analyse de la composition en métaux lourds des lixiviats a mis en évidence l'importante charge métallique de ces percolats. Le fer est le métal le plus abondant (7,77 mg/L). Ceci est vraisemblablement dû au fait que la décharge reçoit des déchets renfermant du fer, surtout les déchets industriels provenant des zones industrielles d’Es-Sénia et d’El-Kerma (Oran, Algérie). Les métaux toxiques présentent des teneurs relativement importantes, avec 1,28 mg/L pour le nickel, 0,6 mg/L pour le cuivre et 0,4 mg/L pour le cadmium. En Algérie, des normes n'ont pas encore été établies pour les lixiviats des décharges, mais nous nous sommes référés à la norme actuelle des rejets d’effluents liquides industriels (JORADP 2006), étant donné que les jus de décharge ou les lixiviats sont comparables à des rejets industriels complexes (Keenan 1983; Parveaud 1993; Renou 2008). Cette norme est de
0,5 mg/L pour le nickel, 0,5 mg/L pour le cuivre et 0,2 mg/L pour le cadmium (JORADP 2006). Quant à la norme internationale, elle est de 0,013 mg/L pour le nickel, 0,07 mg/L pour le cuivre et 0,01 mg/L pour le cadmium (U.S. EPA 2005 cité dans Kurniawan 2006). Il en ressort que le lixiviat étudié accuse des teneurs en nickel, cuivre et cadmium qui dépassent largement les normes algérienne et américaine. La classification des concentrations des métaux lourds de ces lixiviats dans l’ordre croissant est la suivante : Fe>Cu>Zn>Mn et Ni>Cd>Pb>Cr. La teneur en métaux des lixiviats issus de la décharge d’El-Kerma est typique d’une décharge à caractère ménager dominant (Kerbachi et Belkacemi 1994; Khattabi 2002). D’autres paramètres confirment cette évolution temporelle, à savoir : pH basique (8,19), charge métallique relativement moyenne avec une tendance à la baisse, charge minérale moyenne avec une tendance à la hausse.

Traitement des lixiviats par adsorption

Stabilité de la DCO initiale des lixiviats bruts. La Figure 1 montre la stabilité de la DCO initiale (28000 mg d’O₂/L) durant toute la période du traitement (environ 4 mois). On peut ainsi conclure à l’efficacité du système de conservation à froid de l’échantillon du lixiviat (4°C), et par conséquent à l’atténuation de toute activité bactérienne susceptible d’en faire évoluer la charge organique.

Masse optimale du biomatériau. La Figure 2 indique que le taux d’adsorption de la DCO du lixiviat par la sciure du bois croît avec l’augmentation de la quantité d’adsorbant jusqu’à atteindre un palier de saturation : c’est la masse optimale qui marque l’équilibre d’adsorption. En effet, cette masse est de 0,7 g avec un taux d’élimination de 54,27 % pour le biomatériau SB. Quant aux trois autres biomatériaux SB1, SB2 et SB3, la masse optimale est respectivement de 0,4, 0,35 et 0,2 g, avec des pourcentages d’élimination respectifs de 74,95, 80,02 et 84,36 %. Il en ressort que l’abattement de la DCO initiale le plus significatif est obtenu pour la SB3, avec une masse optimale très faible.

Temps de contact optimal. L’examen de la Figure 3 montre que la cinétique d’adsorption est plus rapide dans le cas de la sciure de bois traitée chimiquement à la soude que celle prise à l’état naturel. En effet, pour les SB1, SB2 et SB3, l’équilibre est atteint respectivement au bout de 90, 70 et 40 min, avec des taux d’élimination respectifs de 74,95, 80,02 et 84,36 %. Il en ressort que l’abattement de la DCO initiale le plus significatif est obtenu pour la SB3, avec une masse optimale très faible.
Traitement des lixiviats de décharge

le matériau naturel SB, l’équilibre est atteint après 150 min avec un pourcentage d’élimination réduit à 63,66 %. Ceci indique que l’activation de la sciure à la soude et la normalité de la soude utilisée sont déterminants dans le phénomène d’adsorption de la matière organique.

**pH optimal.** Le taux maximum d’adsorption de la DCO a été obtenu à pH 11,0 pour chacune des quatre formes de sciure de bois et ce taux est le plus élevé dans le cas de la sciure activée à la soude 3 N (Figure 4). Ces résultats démontrent bien que le pH basique, l’activation chimique et la concentration sont les facteurs qui contribuent le plus à optimiser le processus d’adsorption.

 Isothermes d’adsorption. Afin d’apprécier la capacité maximale d’adsorption de la matière organique des lixiviats, exprimée en concentration de DCO, sur la sciure de bois naturelle et traitée chimiquement, les modèles de Freundlich et de Langmuir, sous leur forme linéarisée, ont été appliqués (Ferrandon et al. 1995; Fiset et al. 2000; Marin 2001; Acar et Eren 2006; Hameed et al. 2007; Sciban et al. 2007):

$$\log \left( \frac{Q_e}{Q} \right) = \log (K_F) + \frac{1}{n} \log (DCO)$$

(3)

$$\frac{DCO \cdot Q_e}{Q} (g/L) = \left( \frac{1}{bQ_{max}} \right) + \left( \frac{1}{Q_{max}} \right)DCO$$

(4)

où $K_F$ et $n$ sont des constantes empiriques de Freundlich représentant respectivement la capacité et l’intensité d’adsorption, $Q_{max}$ est la capacité maximale d’adsorption de Langmuir (mg/g) et $b$ est la constante d’équilibre de Langmuir associée à l’énergie d’adsorption (L/mg).

Les isothermes d’adsorption ont été établies à différentes températures (25, 35, 45 et 55°C) et dans les conditions optimales retenues. Plusieurs graphiques ont été obtenus et sont tous de type I, correspondant à une adsorption en monocouche de la charge organique polluante sur le support solide étudié. Seulement deux graphiques seront présentés dans ce travail : ils correspondent aux températures 25 et 55°C (Figure 5). Ces graphiques montrent que les rendements épuratoires les plus importants sont obtenus à la température 55°C, sur sciure de bois activée à la soude 3 N.

Plusieurs courbes de modélisation des isothermes d’adsorption ont été établies aux différentes températures, elles présentent pratiquement la même allure. La Figure 6 montre les courbes des températures 25 et 55°C, pour le meilleur matériau SB3. L’ensemble des résultats, reporté dans le Tableau 2, révèle que la capacité d’adsorption
est maximale, de l’ordre de 100 mg/g, selon le modèle de Langmuir. En effet, celui-ci a donné des coefficients de corrélation, $R^2$, très significatifs et des facteurs de séparation adimensionnels, $R_L$, très favorables (compris entre 0 et 1) (Nomanbhay et al. 2005; Hamdaoui 2006; Ferrero 2007; Hameed et al. 2007; Meena et al. 2008).

Les caractéristiques essentielles des isothermes obéissant au modèle de Langmuir sont souvent décrites par ce facteur adimensionnel de séparation $R_L$ qui indique que l’adsorption est favorable ou pas et qui est défini comme suit (Hall et al. 1966; Kadirvelu et al. 2001; Hamane 2005) :

$$R_L = 1/(1 + bC_i) \quad (5)$$

où $b$ est la constante d’équilibre de Langmuir (L/mg) et $C_i$ représente dans notre cas la DCO initiale du lixiviat brut (DCO$_i$ = 28000 mg d’O$_2$/L).

Figure 5. Isothermes d’adsorption de la matière organique sur la sciure de bois aux températures de 25°C (a) et 55°C (b) et à pH 11.0. Symboles : Sciure de bois naturelle (■) SB, Sciure de bois activée à la soude 1 N (●) SB1, Sciure de bois activée à la soude 2 N (▲) SB2, Sciure de bois activée à la soude 3 N (▲) SB3.

Étude thermodynamique de l’adsorption

Dans le cas d’une réaction chimique, la constante d’équilibre peut être assimilée au coefficient de distribution $K_c$ du soluté (matière organique) entre les quatre formes de sciure de bois et les lixiviats. Les variations de l’énergie libre de Gibbs ($\Delta G$), de l’enthalpie ($\Delta H$) et de l’entropie ($\Delta S$) pour le processus d’adsorption peuvent être obtenues en utilisant les deux équations suivantes (Hamane 2005; Argun et al. 2007; Meena et al. 2008) :

$$\Delta G = -R \, T \, \ln K_c \quad (6)$$

et

$$\ln K_c = (\Delta S/R) - (\Delta H/RT) \quad (7)$$

where $R$ is the gas constant, $T$ is the temperature in Kelvin, $\Delta S$ is the entropy change, $\Delta H$ is the enthalpy change, $\Delta G$ is the free energy change, and $K_c$ is the equilibrium constant for the adsorption process.

Figure 6. Isothermes d’adsorption de la matière organique sur la sciure de bois activée à la soude 3 N (SB3), selon le modèle de Langmuir, aux températures de 25°C (a) et 55°C (b) et à pH 11.0.
Traitement des lixiviats de décharge

Tableau 2. Paramètres équationnels des modèles de Freundlich et de Langmuir de l’adsorption de la DCO du lixiviat sur la sciure de bois naturelle et modifiée chimiquement, à différentes températures

<table>
<thead>
<tr>
<th>Matériaux</th>
<th>T°C</th>
<th>Modèle de Freundlich</th>
<th>Modèle de Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>KF</td>
<td>N</td>
</tr>
<tr>
<td>SB*</td>
<td>25</td>
<td>0,902</td>
<td>1,915</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0,978</td>
<td>1,855</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>1,881</td>
<td>2,097</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>1,883</td>
<td>1,935</td>
</tr>
<tr>
<td>SB1 **</td>
<td>25</td>
<td>2,093</td>
<td>2,056</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>5,263</td>
<td>2,715</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>6,700</td>
<td>2,866</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>7,224</td>
<td>2,328</td>
</tr>
<tr>
<td>SB2 ***</td>
<td>25</td>
<td>1,966</td>
<td>2,234</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>6,076</td>
<td>2,674</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>7,202</td>
<td>2,596</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>8,421</td>
<td>2,099</td>
</tr>
<tr>
<td>SB3 ****</td>
<td>25</td>
<td>4,794</td>
<td>2,132</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>9,607</td>
<td>2,401</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>10,923</td>
<td>2,331</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>16,984</td>
<td>2,140</td>
</tr>
</tbody>
</table>

*SB; Sciure de bois naturelle.
**SB1; Sciure de bois activée à la soude 1 N.
***SB2; Sciure de bois activée à la soude 2 N.
****SB3; Sciure de bois activée à la soude 3 N.

 où ln K représente K dans le modèle de Freundlich et b dans le modèle de Langmuir; R représente la constante des gaz parfaits (8,314 J. mol⁻¹·K⁻¹).


Etude de la cinétique d’adsorption

Cette étude a pour but de déterminer l’ordre et la vitesse de la réaction d’adsorption de la matière organique, en appliquant l’équation de la cinétique du premier ordre de Lagergren, 1898 (Marin 2001; Demirbas et al. 2004; Hamane 2005; Argun et al. 2007; Hameed et al. 2007; Li et al. 2007) sous sa forme linéaire :

\[ \log (Q_e - Q_t) = \log (Q_e) - \frac{k}{2.303} t \]  

où \( Q_e \) et \( Q_t \) sont les capacités d’adsorption respectivement à l’équilibre et à l’instant \( t \) (mg/g) et \( k \) la constante de vitesse d’adsorption (min⁻¹).

Le tracé du \( \log (Q_e - Q_t) \) en fonction du temps permet de déduire la constante de vitesse \( k \) pour une réaction d’ordre 1, comme le montre la Figure 7. Nous pouvons constater que l’évolution de \( \log (Q_e - Q_t) \) en fonction du temps est linéaire et que la cinétique de la réaction d’adsorption dans les quatre cas est donc du premier ordre. La constante \( k \), déduite de la pente de la droite, est égale à 1,86×10⁻², 5,31×10⁻², 5,24×10⁻² et 1,14×10⁻¹ min⁻¹, respectivement pour SB, SB1, SB2 et SB3, avec des coefficients de corrélation \( R^2 \) très significatifs. Ceci plaide en faveur d’une meilleure adéquation de nos résultats avec le modèle de Lagergren pour une réaction d’adsorption du premier ordre.

Essai de traitement successif des lixiviats

Plusieurs essais de traitement successif du lixiviat brut ont été réalisés dans les mêmes conditions opératoires et optimales requises (DCO initiale, régime statique, masse de sciure, temps de contact et pH). Ils ont consisté à faire passer le lixiviat à travers cinq réacteurs disposés en série.

87
Tableau 3. Grandeurs thermodynamiques de l’adsorption de la DCO du lixiviat sur la sciure de bois naturelle et modifiée chimiquement, à différentes températures

<table>
<thead>
<tr>
<th>Matériau</th>
<th>$T^\circ$ (K)</th>
<th>Modèle de Freundlich</th>
<th>Modèle de Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T^\circ$ (K)</td>
<td>$\Delta G^f$ (kJ/mol)</td>
<td>$\Delta S^\theta$ (J/mol.K)</td>
</tr>
<tr>
<td>SB $^a$</td>
<td>298</td>
<td>-256,55</td>
<td>76,85</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>-55,90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-1669,96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-1725,83</td>
<td></td>
</tr>
<tr>
<td>SB1 $^b$</td>
<td>298</td>
<td>-1830,38</td>
<td>117,28</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>-4252,55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-5028,74</td>
<td></td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-5392,52</td>
<td></td>
</tr>
<tr>
<td>SB2 $^c$</td>
<td>298</td>
<td>-1675,46</td>
<td>133,10</td>
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<tr>
<td></td>
<td>308</td>
<td>-4620,32</td>
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<td>318</td>
<td>-5220,07</td>
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</tr>
<tr>
<td></td>
<td>328</td>
<td>-5810,59</td>
<td></td>
</tr>
<tr>
<td>SB3 $^d$</td>
<td>298</td>
<td>-3883,15</td>
<td>121,18</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>-2560,71</td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-6321,16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-7723,52</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ SB: Sciure de bois naturelle.
$^b$ SB1: Sciure de bois activée à la soude 1 N.
$^c$ SB2: Sciure de bois activée à la soude 2 N.
$^d$ SB3: Sciure de bois activée à la soude 3 N.
$^\circ$ T: Température du milieu (K).
$^f \Delta G$: Variation de l’énergie libre de Gibbs.
$^\theta \Delta S$: Variation de l’entropie.
$^b \Delta H$: Variation de l’enthalpie.

Figure 7. Cinétique d’adsorption de la matière organique sur la sciure de bois, selon le modèle de Lagergren. Symboles : Coefficient de corrélation $R^2$: SB ($\bullet$) 0,9899, SB1 ($\bullet$) 0,9754, SB2 ($\bullet$) 0,9794, SB3 ($\blacktriangle$) 0,9667.

Figure 8. Abatement de la DCO du lixiviat au cours du traitement successif. Symboles : Sciure de bois naturelle ($\blacksquare$) SB, Sciure de bois activée à la soude 1 N ($\bullet$) SB1, Sciure de bois activée à la soude 2 N ($\bullet$) SB2, Sciure de bois activée à la soude 3 N ($\blacktriangle$) SB3.
Il ressort de ces essais que la température la plus optimale doit être supérieure à 45°C. En effet, à des températures élevées et dans des conditions optimales d’adsorption, il s’est avéré que pour atteindre un abattement maximal de la DCO, seulement trois réacteurs sont suffisants (Figure 8). L’abattement le plus important a été obtenu dans le cas du traitement successif sur la sciure de bois activée à la soude 3 N : la DCO est passée de 28000 à 330 mg d’O₂/L, soit un abattement de l’ordre de 98 %.

Conclusions

A l’issue de notre travail qui a porté sur la caractérisation et le traitement des lixiviats de la décharge incontrôlée et publique d’El-Kerma (Oran, Algérie), il est permis de tirer les conclusions suivantes :

- Les résultats des analyses physico-chimiques des lixiviats ont révélé une forte charge minérale, métallique et organique. Les valeurs trouvées (CE de 120,3 mS/cm; Cl⁻ de 3379 mg/L; SO₄²⁻ de 1717 mg/L; NH₄⁺ de 2726 mg/L; DBO₅/DCO de 0,17; Ni de 1,28 mg/L; Cu de 0,6 mg/L; Cd de 0,4 mg/L) dépassent largement les normes nationales et internationales. Cela nous a permis de conclure qu’il s’agit d’un lixiviat, et par conséquent d’une décharge, traversant actuellement l’âge intermédiaire et tendant vers celui de la méthanogenèse. Ce lixiviat à forte charge polluante risque de contaminer la nappe phréatique qui circule à des faibles profondeurs (environ 20 m), sous un sol moyennement perméable.

- L’établissement des isothermes d’adsorption de la matière organique sur les différents matériaux envisagés et à différentes températures a démontré une capacité maximale d’adsorption de l’ordre de 100 mg/g lors de l’utilisation de sciure de bois activée à la soude 3 N (SB3), selon le modèle de Langmuir. L’ordre décroissant de la capacité d’adsorption des quatre formes de sciure de bois s’établit comme suit : SB3 > SB2 > SB1 > SB.

- L’étude thermodynamique a montré que le processus de traitement est spontané et endothermique. La cinétique est rapide et obéit au modèle du premier ordre (Lagergren).

- Les essais de traitement successif du lixiviat brut ont donné des rendements épuratoires très satisfaisants (abattement de 98 % de la DCO).

La caractérisation physico-chimique des lixiviats effectuée lors de cette étude permettra d’orienter la filière de leur traitement pour répondre aux normes de rejet les plus strictes. Toutes les méthodes d’étude utilisées dans le cadre de ce travail (chimie analytique, adsorption sur biomatériaux, génie des procédés, hydrogéologie, pédologie, etc.) ont montré un meilleur recouvrement et leur combinaison constitue une bonne méthodologie de fonctionnement et de travail dans le traitement des lixiviats. Cette méthodologie pourrait être transposée à d’autres sites de décharges nationales et internationales ayant les mêmes caractéristiques intrinsèques et extrinsèques.

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Research on the Application of Laccase to the Treatment of Oily Wastewater

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2 Research Institute of Yanshan Petrochemical Co., Ltd., SINOPEC, Beijing 102500, China

The feasibility of using laccase to treat oily wastewater was examined. When only laccase was added to the synthetic oily wastewater, the suitable technological conditions were laccase at 3 U/mL, pH at 6.0, a temperature of 30°C, and a reaction time of 6 h for the initial oil concentration of 120 mg/L. Under those conditions, the rate of oil removal was as high as 69%. The effects of Mg2+, Mn2+, Cu2+, and Fe2+ ions in wastewater on the rate of oil removal using laccase were investigated. The results showed that Cu2+ and Fe2+ ions obviously inhibited the catalytic performance of laccase under the studied concentration. On the other hand, Mg2+ and Mn2+ ions only had slight effects on the rate of oil removal for the range of concentrations studied. A 95% oil removal rate could be obtained when actual wastewaters were treated using laccase with the additive chitosan under the suitable technological conditions.

Key words: laccase, oily wastewater, polyethylene glycol, chitosan, enzyme catalytic treatment

Introduction

Oil that is leaked during the processes of petroleum refining, storage, transportation, and production of petrochemical products as well as the accidental release of oil products may result in contamination of the water environment. Some ingredients of petroleum are organic mixtures containing low boiling-point aromatic hydrocarbon compounds that are toxic to aquatic plants. For example, such mixtures can decrease the content of oxygen in oily wastewater, thereby inhibiting photosynthesis by water plants (Galvão et al. 2006). Some petroleum compounds contain polycyclic aromatic hydrocarbons which are carcinogenic and can severely threaten the health of humans and aquatic animals. Therefore, oily wastewater should not be discharged directly without treatment.

Oil in water can exist as free or suspended oil, dispersed oil, emulsified oil, and dissolved oil. Suspended or dispersed oil can be readily separated from wastewater by simple physical processes. However, emulsified or dissolved oil is more difficult to remove from wastewater. At present, there are several methods for removing emulsified oil and dissolved oil from wastewater, including ozone oxidation, ultraviolet- (UV-) catalyzed oxidation, Fenton reagent, biological degradation, ultrasonic wave oxidation, etc. (Andreozzi et al. 2000; Chang et al. 2001; Badawy and Ali 2006; Galvão et al. 2006; Tezcan et al. 2006). These have some limitations, such as restricted application conditions, high operation costs, corrosion, and recontamination (Braun and Oliveros 1997; Zouboulis and Avranas 2000). Furthermore, these methods are not always effective in removing dilute emulsified oil or dissolved oil. Enzymatic degradation has the advantages of convenient operation, mild reaction conditions, high efficiency, a wide operating range, and the elimination of recontamination, so it may be a good solution to the above problems in the treatment of oily wastewater. Furthermore, because of the high efficacy of immobilized enzyme and the additive enhancement of enzymatic activity, the enzymatic degradation may be a promising economical procedure for industrial applications compared with the conventional physicochemical methods in treating emulsified oily and dissolved oily wastewaters (Durán et al. 2002; Kurian et al. 2006).

Laccase is one of the potential biocatalysts (Srebotnik and Hammel 2000; Mayer and Staples 2002a). It has been reported that laccase can catalyze more than 250 substrates; therefore, it has a broad substrate spectrum and may be especially suitable for the treatment of oily wastewater of complex composition (Setti et al. 1999; Claus 2004). In other words, laccase is different from enzymes that can only catalyze specific substrates, so it may be able to simultaneously catalyze various kinds of compounds in mixtures of oily wastewater. In the past, the applications of laccase were mainly concentrated on the pulp and paper manufacturing industry, especially on aspects of lignin degradation and pulp biobleaching (Ishihara 1980; Li et al. 1999; Wong and Yu 1999; Mayer and Staples 2002b; Barreca et al. 2003). In recent years, the laccase-catalyzed polymerization and precipitation processes were explored for the treatment of various aromatic compounds, such as phenols and anilines (Durán et al. 2002), but they were usually limited to the sole substrate (Ganjidoust et al. 1996; Tsioulpas et al.
As far as we know, there are no reports regarding the application of laccase to the treatment of oily wastewater. Laccases are multicopper-containing enzymes that can catalyze the oxidative conversion of a variety of chemicals. Laccase can couple four one-electron oxidations of the substrates. The various copper centres of laccases drive electrons (Claus 2004). The electrons can be further transferred and attack the substrates (emulsified oil and dissolved oil in the wastewater). The attack may generate radicals that react with each other to form insoluble products, such as dimers, oligomers, and polymers. The insoluble products can be removed from wastewater via precipitation during further treatment processes.

In this paper, laccase was applied to catalyze the oxidation of the oil in wastewater, and the suitable conditions of the laccase-catalyzed oxidation of the oil in wastewater were researched in terms of reaction time, temperature, pH, and laccase concentration. The effects of metal ions on the rate of oil removal were also evaluated. The effects of additives on the laccase-catalyzed oxidation of oil were explored. The rates of oil removal were compared between synthetic oily wastewater and actual oily wastewater.

Materials and Methods

Materials

Laccase (EC 1.10.3.2) was produced by Fluka Co. (Buchs, Switzerland). The laccase activity was quoted as 7.44 U/mg of dry solid. Laccase stock solutions were prepared by dissolving solid laccase in 0.1 mol/L of acetic buffer (pH 4.0), and were stored at a temperature of 4°C. Twice-distilled diesel oil was provided by Yanshan Petrochemical Co., Ltd. (Beijing, China). The synthetic oily wastewater was prepared by emulsifying diesel oil in a 0.2 mol/L phosphate buffer. Characteristics of the synthetic oily wastewater are listed in Table 1.

Petroleum ether (boiling point range: 60 to 90°C), acquired from Changhai Chemical Co. (Beijing, China), had a transmittance of light greater than 80% after being purified. Chitosan (viscosity of 420 centipoises) was produced by Sigma Chemical Co. (St. Louis, Mo.). A chitosan solution of 10 g/L was prepared by dissolving the polymers in a 1% by weight acetic acid solution, and any undissolvable particles were removed from the solution by vacuum filtration. The solution was stored at a temperature of 4°C after preparation. Polyaluminum chloride (PAC) of technical grade was obtained from Fisher Chemical (Fair Lawn, N.J.). The polyethylene glycol (PEG) (average molecular weight 8,000), 3-ethylthiazoline-6-sulfonate (ABTS), and other materials were all of analytical grade.

Analytical Methods

Laccase activity was measured with a colourimetric assay (Beckman Coulter DU530, Fullerton, Calif., U.S.A.) containing 1 mM ABTS substrate, 100 mM citrate buffer (pH 4.0), and a suitable amount of enzyme (0.05 to 0.25 U/mL) (Wolfenden and Wilson 1982; Eggert et al. 1996; Gianfreda et al. 1998; Wong and Yu 1999). Prior to significant substrate depletion, the enzyme activity was proportional to the rate of formation of a coloured product that absorbed light at the wavelength of 600 nm. The unit activity (U) of laccase in this assay mixture was expressed as 1 μmol of the coloured product formed from the ABTS oxidation per minute at a temperature of 25°C.

There are many analytical methods used to determine oil concentrations, such as the extractive-gravimetric method and instrumental methods (e.g., refractometry index determination and UV spectrophotometry). Among them, UV spectrophotometry is the most precise (Zhao et al. 2006; Rajakovic et al. 2007); this is because oil has characteristic absorbance in the ultraviolet range (Verner et al. 2000), and ultraviolet spectrophotometry provides superior precision and reliability. Therefore, oil concentrations in the wastewater were determined using UV spectrophotometry according to a Chinese national standard (Water and Wastewater Monitoring Analysis Committee of Chinese National Environment Bureau 1989). The oil concentration was measured with a UV spectrophotometer (WFZ800-D-A, Beijing Optical Apparatus Factory, Beijing, China) at the wavelength of 225 nm which proved to have the maximum absorption for the oil used. The measurement was taken after the oil in the reaction mixtures or wastewater was extracted with petroleum ether. The rate of oil removal was expressed as the percentage of oil removed in relation to the initial oil amount.

Experimental Procedures

The overall experimental procedures included: preparation of the synthetic wastewater, reaction initiation, reaction

<table>
<thead>
<tr>
<th>Main ingredients</th>
<th>Oil concentration (mg/L)</th>
<th>COD * (mg/L)</th>
<th>Particle diameter of oil (μm)</th>
<th>SS * (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane+cyclide+aromatic compounds</td>
<td>120</td>
<td>2,520–3,240</td>
<td>0.4–80</td>
<td>0.001</td>
</tr>
</tbody>
</table>

*COD = chemical oxygen demand.
*SS = suspended solids.
interruption, flocculation of reaction mixture, and the analysis of oil concentration.

Batch reactions were carried out in glass vials of 250-mL capacity at pH 6.0 (except for the tests on the effects of pH), an oil concentration in the synthetic wastewater of 120 mg/L, different concentrations of chitosan or PEG (which was added before the addition of laccase), and a suitable amount of laccase. The reaction mixtures of the synthetic wastewater, chitosan, and laccase were incubated in a shake bed (HYG-III shake bed, Shanghai Automatic Control Apparatus Factory, Shanghai, China) at 30°C (or at 27 to 75°C to determine the effects of temperature on the rate of oil removal). The pH of the reaction mixtures was adjusted to the desired level (from 2.7 to 9.0) using common buffers, i.e., a 25 mM acetate buffer at a pH of 2.7 to 4.9, and a 25 mM phosphate buffer at a pH of 5 to 9. For experiments involving reactions in the presence of metal ions, stock solutions of Mg²⁺, Mn²⁺, Cu²⁺, and Fe⁺ were prepared using the corresponding sulfate salts. The metal ion concentrations in the reaction mixtures were from 0 to 70 mg/L. For experiments involving PEG, chitosan, Al₂(SO₄)₃, and PAC, the solutions were prepared using deionized water. The concentrations of both PEG and chitosan in the reaction mixtures ranged from 20 to 160 mg/L. The concentrations of both Al₂(SO₄)₃ and PAC in the reaction mixtures were 80 mg/L.

The reaction was initiated by the addition of laccase into the reaction mixtures. The reaction mixture was capped and continuously stirred with a magnetic stirrer at a speed of approximately 140 rpm during the reaction. Our results demonstrated that the oxygen in the reaction mixture and the headspace in the reaction vial did not affect the transformation of the oil (data not shown here).

By adding sulfuric acid into the reaction mixture to adjust the pH of the reaction mixture to 2 or lower, the enzymatic reaction was stopped to test the reaction effectiveness at the required reaction time.

Prior to the analysis of oil concentration, the floc in the reaction mixtures was flocculated with the flocculating agents Al₂(SO₄)₃ (80 mg/L) and PAC (80 mg/L) at a pH of 8.0. Subsequently, the mixture was centrifuged for 30 min at approximately 3,000 rpm. Immediately after the supernatant liquid was poured out, it was analyzed for residual oil concentration with the colourimetric method described above.

**Results and Discussion**

**Effect of pH**

Generally, all enzymes have a suitable working pH value. It was reported that the suitable working pH value of free laccase was from 3.0 to 9.0 (Srebotnik and Hammel 2000). In order to determine the effect of pH on the removal of oil in the wastewater, three sets of reactions (with 3.0 U/mL of laccase, 4.0 U/mL of laccase, and 3.0 U/mL of laccase with 80 mg/L of chitosan) were conducted in which the pH of water sample was varied from 3.0 to 9.0. The results are shown in Fig.1 and indicate that the rate of oil removal was a function of pH. The pH ranges suitable for achieving significant oil removal (reduction of the remaining oil concentrations to 50 mg/L, equivalent to an oil removal rate of 58%) were from 4.5 to 7.2 for laccase at 3 U/mL, from 3.5 to 8.0 for laccase at 4 U/mL, and at all pH levels tested with laccase at 3 U/mL plus chitosan at 80 mg/L. All three sets of reactions reached the highest rate of oil removal at pH 6, which was slightly higher than the reported isoelectric point of laccase (Yaropalov et al. 1994). Thus, all subsequent experiments were conducted at a pH of 6.0.

It has been reported that the mechanism of laccase in catalyzing organic pollutants, such as aromatic compounds, is the conversion of the substrates into free radical products and the coupling reactions of the products leading to polymerization (Durán et al. 2002; Claus 2004). The mechanism of laccase catalyzing oil in wastewater may be similar to that process. Thus, the effects of the pH of the water sample on the rate of oil removal may be attributed to its influence on the state of the functional groups of laccase, and the consequent influence on its ability to attack substrates. Therefore, the pH value changed the action efficiency of laccase on substrates.

**Effect of Laccase Concentration**

The commercially available laccases are very expensive. Therefore, it is important to determine the minimum suitable amount of laccase for achieving a relatively high rate of oil removal from the wastewater.

In order to determine the suitable concentration of laccase, batch experiments were conducted in which the concentrations of laccase added to the water samples was varied from 0 to 4 U/mL. The results are shown in Fig. 2. As expected, the rate of oil removal increased...
Fig. 2. Effect of laccase concentration on the rate of oil removal. The reactions were conducted for 6 h with an initial oil concentration of 120 mg/L, pH of 6.0, and temperature of 30°C.

Fig. 3. Effect of temperature on the rate of oil removal. The reactions were conducted for 6 h with an initial oil concentration of 120 mg/L, laccase concentration of 3 U/mL, and pH of 6.0.

with the increasing concentration of laccase. To achieve a reduction from 120 to 50 mg/L of oil remaining, the minimum laccase concentration required was 1.5 U/mL. To reduce the oil concentration remaining to 30 mg/L (equivalent to a rate of oil removal of 75%), the minimum laccase concentration required was 3.0 U/mL. To make a further reduction of the remaining oil concentration to 28 mg/L (equivalent to a rate of oil removal of 76%), the laccase concentration had to be increased to 4.0 U/mL or more.

The effects of laccase concentration on the rate of oil removal can be attributed to the fact that larger concentrations of laccase can cause the formation of greater amounts of the free radical products and the subsequent coupling-reaction polymers. When the laccase concentration was over 3.0 U/mL, its increase had little effect on the rate of oil removal. The reason could be that the products of polymers can inhibit the generation of free radical products and the laccase-catalyzing reaction. Therefore, the incremental rate of oil removal was inhibited when the concentration of laccase exceeded a certain amount. Therefore, the suitable concentration of laccase in this study was considered to be 3 U/mL.

Effect of Reaction Temperature

The effect of reaction temperature on the rate of oil removal from wastewater for a 6 h reaction time is shown in Fig.3. The results show that the rate of oil removal increased with an increase of temperature from 27 to 50°C. This could be the result of the increased temperature accelerating the formation of the free radical products and the coupling reaction leading to polymerization compared with when the temperature was relatively low. However, a descending tendency of the rate of oil removal was observed above 50°C. This could be the result of the higher temperature leading to inactivation of the laccase, and/or the large quantity of polymers produced blocking laccase from attacking the substrate. Laccase inactivation at high temperatures has already been verified (Kim and Nicell 2006a; Kim and Nicell 2006b).

Although the increase of temperature may cause competition between an increase and decrease of the laccase activity, it can be observed that the rate of oil removal by the laccase catalytic oxidation only changed a small extent (between 69 to 71%) in the temperature range of 30 to 70°C. In other words, the rate of oil removal was still high at this temperature range. Therefore, the process of oil removal from wastewater with laccase showed a broad operational temperature range. Generally, thermal inactivation is irreversible and therefore dangerous to laccase treatment of wastewater. On the other hand, low temperature is both economical and convenient for operation; therefore, the temperature should be as low as possible when the rate of oil removal can be kept high. According to these analyses, the suitable temperature in this case was 30°C.

Effect of Reaction Time

In order to evaluate the effect of reaction time on the oil removal rate, experiments were conducted at various concentrations of laccase. The results are shown in Fig.4. It is observed that the majority of transformation occurred in the initial stage. Within the first 6 h of incubation, oil removal rates of approximately 69, 61, and 45% were obtained at laccase concentrations of 3, 2, and 1 U/mL, respectively. After the initial 6 h, the rate of oil removal was almost constant at all laccase concentration levels tested. Therefore, a reaction time of 6 h should be enough for all concentrations of laccase.
According to the deduction above on the mechanism of laccase catalyzing oil removal, the amounts of free radical products converted from the substrates and of polymers produced by the coupling reactions of the products should increase with the passing of time. Therefore, the rate of oil removal increased with the passing of time. However, after a certain time period, the polymerization products would inhibit the generation of free radical products (Durán et al. 2002) such that the subsequent reactions would also be inhibited. Therefore, the rate of oil removal gradually reached a nearly constant value.

Effect of Metal Ions

Generally, there are some types of metal ions in freshwater or circulating water; therefore, it is necessary to investigate their potential effect on the treatment efficiency of synthetic oily wastewater with laccase. Experiments on the effect of the metal ions Mg$^{2+}$, Mn$^{2+}$, Cu$^{2+}$, and Fe$^{2+}$ on the rate of oil removal were designed with an oil concentration of 120 mg/L, a pH of 6.0, a temperature of 30°C, and a laccase concentration of 3.0 U/mL for 6 h. A series of tests were carried out at metal ion concentrations from 0 to 70 mg/L. The results are shown in Fig. 5.

The results show that all the metal ions had similar effects on the rate of oil removal. Mg$^{2+}$ and Mn$^{2+}$ ions did not strongly influence the rate of oil removal. At low ion concentrations, it can be observed that the rate of oil removal decreased a little with the increase of the Mg$^{2+}$ or Mn$^{2+}$ ion concentration, and the rate of oil removal almost kept constant when the ion concentration was higher than 30 mg/L. The Fe$^{2+}$ or Cu$^{2+}$ ion strongly decreased the rate of oil removal at all ion concentrations. Even though the concentration of Fe$^{2+}$ was as low as 5 mg/L, it caused a 7% decrease of the rate of oil removal. Therefore, Fe$^{2+}$ or Cu$^{2+}$ may restrict the actual application of laccase in the treatment of oily wastewater. The mechanisms of metallic ions inhibiting the removal of oil with laccase are not fully understood. However, in the case of copper and iron ions, it has been reported that these ions could interrupt the electron transport systems of laccase and lead to inhibition of substrate conversion (Torres et al. 2003).

Optimization of Additive Concentrations

Laccase is a major cost component of the water treatment process. Therefore, reductions in the laccase concentration used can promote cost competitiveness of the laccase-catalyzed treatment. Many investigations have reported that some additives can improve catalytic efficiency by forming a protective layer in the vicinity of the active centers of the enzyme and restrict the attack by radicals formed in the catalytic reaction (Vachoud et al. 2001; Delanoy et al. 2005; Modaressi et al. 2005). In recent years, PEG and chitosan were widely studied and applied because they consist of nontoxic organic compounds and are harmless to humans (Harris 1992; Wu et al. 1993).

In order to enhance the effectiveness of laccase performance and determine the suitable additive concentration during the treatment of synthetic oily wastewater, parallel experiments were conducted with laccase in the presence of the additives PEG or chitosan at a laccase concentration of 3 U/mL, reaction time of 6 h, pH of 6.0, oil concentration of 120 mg/L, and additive concentrations in the range of 0 to 160 mg/L.

The results are shown in Fig. 6. Other experiment results showed that almost no oil was removed when the additives were used alone without the addition of laccase. As shown in Fig. 6, PEG slightly decreased the rate of oil removal with laccase. Therefore, PEG has a little inhibition on laccase catalysis of synthetic oily.
wastewater under our conditions. In contrast to its strong ability to protect peroxidase (Wagner and Nicell 2002), PEG failed to protect laccase here; this could be attributed to the different nature of the oxidized products of these two enzymes.

On the other hand, a significant enhancement in catalytic efficiency was obtained with chitosan as an additive. When the mass ratio of chitosan/oil was in the range from 0 to 0.67, the rate of oil removal was significantly enhanced with the increase of the amount of chitosan. The rate of oil removal gradually reached its maximum value of 84% at the mass ratio of chitosan/oil of 1.0. Further addition of chitosan resulted in a slight reduction of the rate of oil removal, which is in accordance with the result reported by Cheng et al. (2006). When the mass ratio of chitosan/oil was 0.67, the rate of oil removal reached 82%, which was nearly 98% of its maximum value. Therefore, the chitosan addition over the mass ratio of chitosan/oil of 0.67 was unnecessary.

The incremental behaviour of chitosan on the removal of oil with laccase may be associated with the reduction of enzyme inactivity caused by an interaction of chitosan with the inactivity products.

**Comparison Between the Synthetic Wastewater and Actual Wastewater**

To compare the oil removal effect of laccase in synthetic wastewater versus actual wastewater, parallel batch experiments were conducted under the same conditions of laccase concentration (3 U/mL), reaction time (6 h), and pH (6.0). One of the actual wastewaters studied was generated from the production processes of a petroleum product, and had an oil concentration of 75 mg/L. The other actual wastewater was the circulating water of an oil refinery and had an oil concentration of 89 mg/L. Both kinds of actual wastewater had lower concentrations of oil than that of the synthetic wastewater, so pure oil was added to them so that they had the same total oil concentration as that of the synthetic wastewater of approximately 120 mg/L. The results of the experiments are shown in Fig. 7. When only laccase was added, it can be seen that the rate of oil removal from the synthetic wastewater was only 69%, whereas removal from the two actual wastewaters was 80 and 88%, respectively.

In the experiments involving the actual wastewater, increments of the rate of oil removal were obtained. Reduced treatment efficiencies of oil removal were observed for the synthetic wastewater samples. One possible explanation is that some wastewater components could provide a reactive cosubstrate thereby facilitating the removal of the less reactive oil, just like the mechanism mentioned in Roper et al. (1995). Another possible explanation is that protective species in the actual wastewater components protect the enzyme from inactivation by the polymer products. In other words, the enzyme inactivation would be suppressed by protective species in actual wastewater because the inactivating products may interact with the protective species during the reaction process. But it was difficult to analyze the protective species because the wastewater components were too complex.

When both laccase and chitosan were added at the mass ratio of chitosan/oil of 0.67, the rate of oil removal from the synthetic wastewater increased to 82%, whereas removal from both types of the actual wastewater increased to 95%. Therefore, chitosan can enhance the rate of oil removal by laccase in all types of wastewater tested, which may be attributed to the interaction of chitosan and certain components in the actual wastewater.

Different oil removal efficiencies were reported recently for different removal methods of various kinds of oil. After 70 h of treatment, the largest reduction in COD (chemical oxygen demand) was only 57% by electrochemical technology for electrolysis of an oily sample (Santos et al. 2006). The COD removal efficiency reached the range of 62 to 86% on oil-grease by electrocoagulation accompanying with H\textsubscript{2}O\textsubscript{2} and a coagulant-aid (Tezcan et al. 2006). The oil removal efficiency reached as high as 99% with the photo-Fenton process for the degradation of the diesel. However, the process needs the combined action of H\textsubscript{2}O\textsubscript{2}, ferrous ions, and UV radiation (Galvão et al. 2006); the consumptions of the H\textsubscript{2}O\textsubscript{2}, ferrous ions, and UV radiation power may raise its cost. The method considered in the present study does not require power consumption. The laccase acting as a catalyst can be immobilized on a substrate and be reused in the future industrial process, so the 95% efficiency of oil removal is satisfactory.
Conclusions

Treating oily wastewater using laccase was feasible. When only laccase was added to the synthetic oily water, the suitable technological conditions were laccase at 3 U/mL, pH at 6.0, and a temperature of 30°C, and a reaction time of 6 h for an initial oil concentration of 120 mg/L. Under these conditions, the rate of oil removal was as high as 69%.

At all ranges of concentration tested, the Mg^{2+} or Mn^{2+} ion in the wastewater slightly inhibited the laccase catalytic process, but Cu^{2+} or Fe^{2+} ion obviously inhibited the process. Significant concentrations of Cu^{2+} or Fe^{2+} ion may restrict the actual application of laccase in treating certain oily wastewater.

Of the additives studied, PEG slightly inhibited the oil conversion with laccase, but chitosan enhanced the conversion. When the mass ratio of chitosan/oil was 0.67, the rate of oil removal reached as high as 82%. Because chitosan is biodegradable and nontoxic, it can be a good additive for the treatment of oily wastewater with laccase.

The rate of oil removal of 95% could be obtained when the actual wastewater was treated with both laccase and the chitosan additive under the optimal conditions with an initial oil concentration of 120 mg/L.

Acknowledgment

The authors wish to thank the Research Institute of Yanshan Petrochemical Co., Ltd., SINOPEC (Beijing, China) for financial support.

References


Santos MRG, Goulart MOF, Tonholo J and Zanta CLPS. 2006. The application of electrochemical technology to the remediation of oily wastewater, Chemosphere, 64: 393-9.


Received: 8 January 2009; accepted: 9 July 2009.
In a case study, this paper responds to increasing public interest in water quality issues by investigating chemical changes as water passes through a domestic water hot water system. Elemental changes were measured by simultaneous analysis of the incoming and outgoing water streams and the deposited sediment from an electric water heater tank. The results may alter some long-held beliefs. The collected and dried sediment from the tank was analyzed for thirty common elements by inductively coupled plasma and atomic absorption techniques. Of the 25 elements found, the dominant seven in order of concentration were magnesium, aluminum, copper, zinc, manganese, iron, and sodium, as well as some surprising traces of other elements. The cold water input and the heated output were also analyzed for thirteen measurable elements. In the heated water output, magnesium had a massive 151% increase in concentration, followed by much more modest increases shown by arsenic, calcium, lead, potassium, silicon, and strontium. None of these mass balance changes compromised the potability of the water. The six elements, aluminum, boron, copper, iron, manganese, and sodium, showed decreases in aqueous concentrations on heating, thereby improving the water quality.

**Key words:** water heater sediment, drinking water quality, elemental analysis

### Introduction

The incentive for this project was a curiosity about the composition and mechanism of formation of the sediment which gradually accumulates on the bottom of in-tank electric water heaters. If this accumulation becomes sufficient to reach or cover the lower electric heating element it can lead to premature element failure. This is why in-tank water heater suppliers recommend periodic sediment removal.

Preliminary work determined that some of the chemical elements that accumulated in the sediment were at concentrations below the detection limits of our analytical methods, especially for the incoming cold water and the hot product water. Initially it was anticipated that precipitation of sediment from components present in the cold water input would decrease the concentrations of elements remaining in the hot water. This expectation was supported by the experience of those responsible for local water safety who have no interest in the analysis of hot water tank sediments since their removal is not likely to cause a health problem. Those chemicals found in the sediment would have been substantially removed from the cold water by precipitation in the tank.

### Recent Background

Although many references support the common occurrence of sediment formation in electric (and other) hot water heaters (e.g., Oregon Department of Energy 2008), no reports of the simultaneous analysis of incoming cold water, heater sediments, and hot water output were found. Related analytical data from the incoming drinking water, and of the total residue from evaporation to dryness of a litre of the supply water, have been reported (Rajković and Stojanović 2001; Rajković et al. 2003). However, the total solids obtained by evaporation of the supply water would not be expected to have the same composition as heater sedimented material since this would be strongly affected by the relative solubilities of the component salts present in the water supply. In a pair of related papers no water samples were analyzed directly (Rajković et al. 2004; Rajković et al. 2008). Instead, the concentrations of the solutes present in the water supply were inferred from the composition of evaporation residue combined with crystal structure work, and extraction of radionuclides from the residue. Whatever results one might obtain by these methods, the sedimentation processes occurring could be anticipated to decrease the concentrations of the solutes found in the heated water, as compared with the respective concentrations in the solute of the incoming mains water, from mass balance considerations alone. The four papers cited above did not measure the content of the heated water output. Yet a quantitative knowledge of these changes could be helpful to decide whether to use hot or cold tap water in the preparation of hot beverages or cooking of foods.

### Source Water Supply

The source raw water for the study was obtained from the treated mains water supply for the Greater Victoria urban area which services a population of about 319,000 (CRD 2006a). This supply is derived mainly from the Sooke Lake Reservoir located in the Greater Victoria
Water Supply Area, about 30 km northwest of the city (CRD 2007). The watershed is a forested area of about 11,000 hectares, protected from public access, that provides a clean catchment area to supply the rock-lined reservoir.

The large main reservoir capacity of 91,514 ML (20.1 billion Imperial gallons) provides a reliable water supply for Greater Victoria, and supported the feasibility of this project by providing a stabilized water source with no more than minor changes in the dissolved and suspended solids content during the relatively long term of this test. This supply is disinfected first by irradiation with ultraviolet light (Roxborough et al. 2006), followed by dosing with 1.6 mg/L (usually) chlorine and then ammonia to form chloramine which provides residual disinfection during the many kilometres to the final supply and distribution areas. This was the piped drinking water source that fed the electrically-heated hot water tank during the 30 month period of the test.

**Material and Methods**

**Tank Operation**

Electric hot water tanks generally function as follows. Cold water is added near the bottom and hot water is drawn off the top (Fig. 1). Two thermostated electrical elements, one about 25 cm above the bottom and the other about 25 cm below the top of the tank, are used one at a time to heat the water. A stout magnesium (sometimes aluminum) rod provides cathodic protection. A drain tap is provided for cleaning.

The test was started at the time of installation of a new 170-L (37.5-Imp. gal), 3,000-watt, vitreous enamel-(glass-) lined steel household water heater on February 3, 2004. This step decreased the risk of variables that might be attributable to an aging water heater. Connecting pipes were copper with tin-soldered joints. The thermostats were set at 53°C and the heater operated normally until July 23, 2006, approximately 30 months. Then the power and cold water supplies were turned off for removal of sediment from the tank; capture in new 20-L plastic buckets was begun by a procedure similar to that previously described (B.C. Hydro 2005). Details of the actual methods used are described below.

**Sediment Collection Details**

Sediment collection with a minimum number of repetitious stages was started by opening a hot water faucet in the house located higher than the tank top to provide an air intake. Opening the bottom drain faucet of the tank delivered a clear water discharge. Gravity draining of the tank was continued slowly so as to leave the sediment undisturbed. The exit stream remained free of turbidity until a depth of about 25 cm of water remained in the tank. At this point the higher hot water faucet was closed and the cold water input supply was fully reopened to obtain a forceful stream of water entering the tank to cause vigorous mixing of the sediment with the supernatant water. The (now) highly turbid stream of discharge water containing sediment was collected in new plastic buckets until the tank water level rose to about 25 cm (about two minutes). Then the cold water supply was shut off and collection continued until the water level in the tank dropped to about 20 cm again. At this phase the slowing discharge rate caused a gradual decrease in turbidity as the water level in the tank dropped. The cold water supply was turned on again and the whole process repeated seven times, at which time the water collected from the lower tank faucet was clear as collected, even under forceful discharge. This was taken to indicate that sediment removal was essentially complete.

The medium brown-coloured solid sediment collected completely settled out in a bucket after standing for four to six minutes. The settled layers from the collection buckets were combined and settled to a 2.5-cm layer in a new 250-mL polyethylene bottle. Wet weight as collected was 134.4 g. About 0.5 g of this wet sediment was placed in a plastic capped vial for later wet microscopic examination. The rest of the sediment was partially dried in an oven at 30°C and 1 atm to a constant weight of 82.1 g, which took 72 hours. Additional heating at 105°C gave 65.8 g of fully dried sediment. This was carefully mixed and then a 10.00 g sample was submitted for sediment analysis.

Cold and hot water samples were collected in clean one-litre glass bottles with new plastic-lined caps. Collections were taken on October 10, 2006, from the closest faucets to the water heater after wasting water.
at full flow for a minute, then rinsing each bottle three times before collection. The samples were immediately chilled to 5°C, delivered to the analyst, tested for pH and hardness, and scanned for 30 elements within three days of delivery.

**Analytical and Photomicrography**

Analyses were conducted by MB Laboratories Ltd., Sidney, British Columbia. Percent organic matter of the fully dried sediment was determined by a combustion test of a small sample. The scan for 30 elements in the dried sediment was conducted by digesting a measured sample in 50% aqueous aqua regia on a hot plate set at low heat to avoid spattering, while the volume was taken down to about 5 mL. The sample was filtered to remove any trace of residual sediment and then passed through a Perkin Elmer Optima 2000D Inductively Coupled Plasma (ICP) instrument and a Perkin Elmer Analyst 700 Atomic Absorption Spectrophotometer (AAS) for metal concentration readings. Water samples were prepared for analysis by acidification of a 50-mL sample of each with 1 mL of 50% aqueous aqua regia and then heating in a microwave oven to optimize dissolution. The treated samples were then filtered if necessary, and the clear solutions fed to the ICP and AAS for metal concentration readings. Appropriate standards, blanks, controls, and duplicates were run to maintain confidence in the results.

Photomicrography was conducted on a Wild Microscope Model M 420, equipped with a an Apozoom type 400076 objective lens, RT ICE Spot lighting (Diagnostic Instruments Ltd.), and a Fiber-Lite fibre optic high intensity illuminator MI-150 (Dolan-Jenner Industries). The photographs of the smaller particles comprising most of the sediment were obtained directly without image processing. Sharp images of the full thickness of the larger particles were obtained by focusing on steps of about 0.05-mm thick slices and then combining the thin sharp images to single ones with the help of Photoshop CS2 software using an A OPEN PC-1 Intel (R) Pentium computer.

**Results and Discussion**

**Physical Aspects of Hot Water Tank Sediment**

The 65.8 g of sediment collected was much less than anticipated from the 30 month accumulation period. Microscopic examination of the sediment of wet or dry sediment samples might have been able to distinguish any microbiota present, but was not feasible. However, it did establish that the bulk of the sediment (ca. 99.5%) was comprised of a reddish-brown, agglomerated friable solid with whitish patches, with a particle size range of about 0.01- to 0.1-mm in diameter (Fig. 2a). By hand sorting, about 20 much larger and whiter pieces of this friable solid were separated for close examination. These had the appearance and texture of agglomerated smaller whitish particles, which appeared to be crystalline on microscopic examination. They ranged in size from 1- to 2-mm in diameter, and were much whiter than the main component of the sediment (Fig. 2b).

![Fig. 2. Photomicrographs of fractions of the hot water tank sediment. (a) A representative sample of the smaller-sized component of the sediment. (b) Photomicrograph of about 1/4 of the larger-sized, paler-coloured particles hand picked from the sediment.](image-url)
Reservoir operator analyses in 2005 gave 1.0 mg/L for suspended solids (CRD 2006c). If we assume that the accumulated sediment arose only from the reported suspended solids, then we would expect to have obtained 19.8 to 25.0 g of sediment (19.8 m³ × 1,000 L/m³ × 1.0 mg/L ÷ 1,000 mg/g). This is only about a third of the 65.8 g of dry sediment weight collected, but a similar order of magnitude.

Suspended solids in surface waters with low dissolved solids are often derived largely from planktonic (microbiotic) sources. If present, this fraction would have been oxidized during the combustion step conducted prior to the 30 element analysis, which established that the organic fraction of the sediment was 21.7% of the 65.8 g total dry weight. This amounts to 14.3 g of the total dry weight of sediment collected, quite close to the 19.8 to 25.8 gram range calculated from the 1.0 mg/L suspended solids in the mains water. Therefore, the occasional rise in plankton growth occurring in the Sooke Lake Reservoir can be accommodated by the combustion test result.

It was more difficult to explain that the inorganic fraction comprised 78.3% of the total sediment collected from the Greater Victoria water supply since this supply contains only about 25 mg/L of total dissolved solids, much less than the values of 100 to 370 mg/L common to a number of North American municipal source waters, (e.g., Lange 1969; Health Canada 1991). On this basis very little would have been expected to settle out of the water as insoluble matter during heating. Clearly some chemistry has to be involved to explain this.

### TABLE 1. Thirty element analyses of hot water tank sediment, cold water feed, and hot water output

<table>
<thead>
<tr>
<th>Measured elements</th>
<th>Dried tank sediment (µg·g⁻¹)</th>
<th>Cold water sample (mg·L⁻¹)</th>
<th>Hot water sample (mg·L⁻¹)</th>
<th>Canadian drinking water limits (mg·L⁻¹)</th>
<th>Hot water concentration (% of Potability Guidelines)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>21,200</td>
<td>0.115</td>
<td>0.085</td>
<td>100 µg·L⁻¹</td>
<td>85</td>
</tr>
<tr>
<td>Antimony</td>
<td>&lt;0.001</td>
<td>&lt;0.500 µg·L⁻¹</td>
<td>&lt;0.500 µg·L⁻¹</td>
<td>6.00 µg·L⁻¹</td>
<td>—</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.917</td>
<td>0.775 µg·L⁻¹</td>
<td>0.857 µg·L⁻¹</td>
<td>10.0 µg·L⁻¹</td>
<td>8.6</td>
</tr>
<tr>
<td>Barium</td>
<td>1.28</td>
<td>&lt;0.009</td>
<td>&lt;0.009</td>
<td>1.00</td>
<td>—</td>
</tr>
<tr>
<td>Beryllium</td>
<td>0.18</td>
<td>&lt;0.003</td>
<td>&lt;0.003</td>
<td>NL d</td>
<td>—</td>
</tr>
<tr>
<td>Boron</td>
<td>36.8</td>
<td>0.146</td>
<td>0.13</td>
<td>5.00</td>
<td>2.6</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.286</td>
<td>&lt;0.100 µg·L⁻¹</td>
<td>&lt;0.100 µg·L⁻¹</td>
<td>5.00 µg·L⁻¹</td>
<td>—</td>
</tr>
<tr>
<td>Calcium</td>
<td>526</td>
<td>5.62</td>
<td>6.13</td>
<td>200</td>
<td>0.31</td>
</tr>
<tr>
<td>Chromium</td>
<td>1.85</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>0.050</td>
<td>—</td>
</tr>
<tr>
<td>Cobalt</td>
<td>4.04</td>
<td>&lt;0.020</td>
<td>&lt;0.020</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Copper</td>
<td>12,300</td>
<td>0.189</td>
<td>0.118</td>
<td>1.00</td>
<td>11.8</td>
</tr>
<tr>
<td>Gold</td>
<td>0.127</td>
<td>&lt;0.040</td>
<td>&lt;0.040</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Iron</td>
<td>1,610</td>
<td>0.057</td>
<td>0.051</td>
<td>0.300</td>
<td>17</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>&lt;0.020</td>
<td>&lt;0.020</td>
<td>&lt;0.020</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Lead</td>
<td>18.2</td>
<td>0.557 µg·L⁻¹</td>
<td>0.635 µg·L⁻¹</td>
<td>10.0 µg·L⁻¹</td>
<td>6.6</td>
</tr>
<tr>
<td>Magnesium</td>
<td>26,500</td>
<td>0.99</td>
<td>2.49</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Manganese</td>
<td>2,100</td>
<td>0.006</td>
<td>0.005</td>
<td>0.050</td>
<td>10.8</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>&lt;0.020</td>
<td>&lt;0.020</td>
<td>&lt;0.020</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Nickel</td>
<td>14.4</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>245</td>
<td>&lt;0.065</td>
<td>&lt;0.065</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Potassium</td>
<td>18.5</td>
<td>0.1</td>
<td>0.106</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Scandium</td>
<td>0.194</td>
<td>&lt;0.050</td>
<td>&lt;0.050</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Silicon</td>
<td>361</td>
<td>1.17</td>
<td>1.22</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Silver</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>0.050</td>
<td>—</td>
</tr>
<tr>
<td>Sodium</td>
<td>1,390</td>
<td>1.84</td>
<td>1.7</td>
<td>200</td>
<td>0.85</td>
</tr>
<tr>
<td>Strontium</td>
<td>1.18</td>
<td>0.016</td>
<td>0.018</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Titanium</td>
<td>3.68</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Tungsten</td>
<td>8.19</td>
<td>&lt;0.050</td>
<td>&lt;0.050</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Vanadium</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>NL</td>
<td>—</td>
</tr>
<tr>
<td>Zinc</td>
<td>3,570</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>5.00</td>
<td>—</td>
</tr>
</tbody>
</table>

| Hardness e         | —                              | 18.1                        | 25.5                      | 0–75 f                                 | —                                                |
| pH                 | —                              | 7.15                        | 8.69                      | 6.5 to 8.5                             | —                                                |

---

a Units in mg·L⁻¹ except where otherwise stated.


Blank (—) denote "no data."

c NL = none listed.

e Hardness (mg·L⁻¹ CaCO₃).

f Generally the concentration range considered to be “soft.”
Interpretation of Sediment Composition

Five of the thirty elements looked for in the sediment were present at concentrations below their analytical detection limits. With detection limits given in parentheses, these were antimony (<0.001 μg/g), lanthanum (<0.02 μg/g), molybdenum (<0.02 μg/g), silver (<0.010 μg/g), and vanadium (<0.010 μg/g) (see Table 1).

The element cations that could play a role in hardness of water, namely aluminum (at 21.2 mg/g), calcium (0.526 mg/g), iron (1.61 mg/g), and magnesium (26.5 mg/g), were all present at quite high concentrations. Electrostatic forces between these di- and trivalent cations would be expected to have a stronger tendency to form insoluble salts with the di- and trivalent anions present in the supply water than most of the other measured elements on this list (see Table 2), and in the process, would preferentially take these salts out of solution (e.g., Lide 2006).

The magnesium concentrations in the sediment and in the hot water stream were the highest of the cations measured. These large increases in magnesium concentrations must have come primarily from the magnesium anode in the water heater. Its measured concentration in the cold water supply was 0.99 mg/L, much less than the 2.49 mg/L present in the hot water. As the magnesium anode dissolves, it decreases the corrosion risks from any less active metals present from the 2.37 volts cathodic protection provided by this process (equation 1):

$$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg} - 2.37 \text{ volts} \quad (1)$$

Any other exposed metal with a lower reduction potential such as iron, which might become exposed to the hot water through formation of a pinhole in the baked vitreous enamel (glass) lining of the water heater will be prevented from going into solution because of the presence of the much higher reduction potential of magnesium (see Table 3).

The high reduction potential of the magnesium could also have contributed to the removal of any dissolved metals already present in the cold water supply, if they lie below magnesium in the electromotive series. The relevant metals which may be involved in this process are those from our 30 element list that lie below magnesium in this series. All of the metals with reduction potentials less than magnesium increased in concentration in the sediment, and those with higher reduction potentials decreased in concentration in the sediment, as shown by Table 3.

An example of the efficiency of this technique is verified by the commercial process used to recover copper from an aqueous acidic solution of cupric ion. Finely divided elemental copper is recovered from the aqueous solution by passing this over a bed of scrap iron (Hocking 2006). The iron, having a higher reduction potential than copper, gives up 2 or 3 electrons to become oxidized to soluble ferrous or ferric ions, which go into solution (equations 2 and 3):

$$\text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2 \text{e}^- \quad (2)$$

$$\text{Fe}^0 \rightarrow \text{Fe}^{3+} + 3 \text{e}^- \quad (3)$$

### TABLE 2. Median concentrations of significant nonmetallic inorganic chemicals in treated water below Japan Gulch for 2005

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Median value (μg L⁻¹)</th>
<th>Derived ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia, total</td>
<td>270.6 as N</td>
<td>H₂N⁺</td>
</tr>
<tr>
<td>Bromide</td>
<td>4 as Br</td>
<td>Br⁻</td>
</tr>
<tr>
<td>Chloride</td>
<td>3,570 as Cl</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>Cyanide</td>
<td>&lt;20 as CN</td>
<td>CN⁻</td>
</tr>
<tr>
<td>Fluoride</td>
<td>14 as F</td>
<td>F⁻</td>
</tr>
<tr>
<td>Nitrate</td>
<td>24.1 as N</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>Nitrite</td>
<td>&lt;0.3 as N</td>
<td>NO₂⁻</td>
</tr>
<tr>
<td>Nitrogen, total</td>
<td>345 as N</td>
<td>misc.</td>
</tr>
<tr>
<td>Phosphate, total</td>
<td>5.34 as P</td>
<td>PO₄³⁻</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1,580 as SO₄</td>
<td>SO₄²⁻</td>
</tr>
</tbody>
</table>

* Selected from data available from CRD (2006b).
* 2005 range was 177.6 to 432.9 μg·L⁻¹ as N.
* These concentrations are very low relative to potability guidelines, see (FTP Committee on Drinking Water 2008) and (Willms and Shier 2006).
* 2005 range was 6.0 to 60.4 μg·L⁻¹ as N.

### TABLE 3. Element mass ratios in cold water, related to element reduction potential position in the electromotive series

<table>
<thead>
<tr>
<th>Element</th>
<th>EMFS b</th>
<th>F°red (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium</td>
<td>0.19</td>
<td>-2.92</td>
</tr>
<tr>
<td>Strontium</td>
<td>0.74</td>
<td>-2.89</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.09</td>
<td>-2.87</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.76</td>
<td>-2.71</td>
</tr>
<tr>
<td>Magnesium</td>
<td>27</td>
<td>-2.37</td>
</tr>
<tr>
<td>Aluminum</td>
<td>184</td>
<td>-1.67</td>
</tr>
<tr>
<td>Manganese</td>
<td>35</td>
<td>-1.05</td>
</tr>
<tr>
<td>Zinc</td>
<td>n.d.</td>
<td>-0.763</td>
</tr>
<tr>
<td>Iron</td>
<td>28</td>
<td>-0.441</td>
</tr>
<tr>
<td>Lead</td>
<td>33</td>
<td>-0.126</td>
</tr>
<tr>
<td>(Pt) hydrogen</td>
<td>-0.000</td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>1.2</td>
<td>(-0.54) d</td>
</tr>
<tr>
<td>Copper</td>
<td>65</td>
<td>-0.34</td>
</tr>
<tr>
<td>Gold</td>
<td>n.d.</td>
<td>-1.42</td>
</tr>
</tbody>
</table>

* Appropriate element reduction potentials selected from Lide (2006).
* b Mass Fraction in Sediment + Mass Fraction in Solute of Cold Water

* n.d. = no data; concentrations in cold and hot water were below analytical detection limits.

* The only nonmetal tabulated.
At the same time, cupric ion is reduced by these electrons to form finely divided elemental (or "cement") copper, which settles out of solution for later recovery (equation 4):

\[
\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}^0 \quad (4)
\]

The two steps are accomplished with an overall iron consumption efficiency of 30 to 70% of theoretical.

The concentrations of several elements of interest were found to be below detection limits in both of the aqueous streams, yet were found in measurable concentrations in the sediment, e.g., copper (12.3 mg/g), gold (0.127 μg/g), lead (18.2 μg/g), and zinc (3.57 mg/g). These results reinforce the potential value of dried sediment analysis alone for the detection of some of the important health-related elements present in a water supply. These data also suggest that parts of the watershed might be located in a metalliferous bedrock area, e.g., the Leech River (Payle 1990).

**Elements Present in the Cold Water Supply**

The thirty element analysis of both the cold water supply and the hot water in the tank gave measurable results for only thirteen elements because of the low concentrations present (see Table 1). The concentrations of the remaining 17 elements tested were well below the direct detection limits of the methods used. Again, this information reinforces the value of analysis of hot water tank sediment to provide a more sensitive measure of the presence of some additional priority elements in the water supply, such as cadmium and chromium.

**Behaviour of the Elements at the Sediment–Cold Water Supply Interface**

To obtain leads as to the mechanisms which might be operating at the junction of the sediment–cold water supply interface (see Fig. 1), it was instructive to consider the ratios of the calculated mass fractions of each of the measured element concentrations in the sediment, as compared with the calculated mass fractions for each of the same measured elements in the solute of the initial mains cold water.

The sediment element mass fraction was found to be substantially higher than the mass of the same element mass fraction present in the solute of the cold water for the following five elements (mass fraction ratios given in parentheses): aluminum (27), iron (4.1), lead (4.8), magnesium (3.9), and manganese (51) (Table 4). For these elements, mechanisms which primarily cause electrochemical deposition or chemical precipitation into the sediment must be operating.

On the same basis copper, with a 0.95 sediment mass fraction to cold water solute mass fraction ratio, is approximately 1:1, or neutral in this respect. The tendency for copper to precipitate by cementation under hot water tank conditions is high, and must be balanced by a nearly equivalent rate of leaching from the sediment to give this outcome.

The seven remaining elements which were present at substantially lower sediment mass fractions to cold water solute mass fractions were: arsenic (0.17), boron (0.0037), calcium (0.015), scandium (0.000284), silicon (0.045), sodium (0.11), and strontium (0.011). For these, electrochemical stripping or chemical leaching processes must be dominant to decrease their concentrations in the sediment to this extent.

**Effects of Heating the Cold Supply Water**

The thirty element analysis of the hot water output sample also gave measurable results for the same 13 elements as for the cold water sample (see Table 4).

Some deposition mechanisms of the elements found in the sediment can be explained. For example, calcium could be initially present as the soluble bicarbonate in the cold feed water. On heating, the bicarbonate could decompose to deposit the insoluble calcium carbonate (permanent hardness) into the sediment (equation 5):

\[
\text{Ca(HCO}_3\text{)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad (5)
\]

Magnesium carbonate is about ten times more soluble at ambient temperatures than the calcium salt, so it would be anticipated to play a lesser role in this process.

A concentration of 26 ppm from December 30, 1971 for Sooke Lake represents the only available bicarbonate analysis for these waters (Ker and others 1971 Personal communication). Dividing the 91.11 g molar mass of calcium carbonate by the 51.03 g molar mass of bicarbonate ion and multiplying by the 26 ppm (a unit very close to mg/L under these conditions) measured concentration of bicarbonate ion in Sooke Lake gives a maximum possible concentration of calcium carbonate from this process of 46.4 mg/L. However, the 50°C water temperature is less than optimum for complete reaction by this scenario. So it is estimated that half or less of the maximum possible, or less than 23 mg/L of calcium carbonate, could be a reasonable product concentration.

The permanent hardness in calcium carbonate equivalents rose from 18.1 mg/L in the cold supply water to 25.5 mg/L in the hot water output, both at 17°C (see Table 1). This rise of 7.4 mg/L would suggest that our rough estimate of the contribution of thermal decomposition of the hot aqueous bicarbonate to the concentration of calcium carbonate in the hot water was a little high. At the same time, the pH in the supply water rose from 7.15 to 8.69 in the hot water, also at 17°C. The direction of this pH change is consistent with a change of part or all of the original bicarbonate salt(s) to carbonate salts, because carbonate is the more basic anion. As examples of this, 0.1 N aqueous sodium bicarbonate has a pH of 8.4, while 0.1 N sodium carbonate gives a pH of 11.6, and saturated aqueous calcium carbonate has a pH of 9.4 (Weast 1975).
Consider first, the more favourable side of the process, that the elements that are accumulated in the sediment have been removed from the cold water by heating it. The following six elements showed modest decreases in the hot water compared with the cold water feed: aluminum (by -26%), boron (-11%), copper (-38%), iron (-11%), manganese (-17%), and sodium (-8%), averaging -18.5% (Table 5). These reductions would have the effect of actually improving the potability of the water.

For a consistency check, the elements whose concentrations decreased in the cold to hot water transition should show an increase in the mass fractions present in the sediment compared with the cold water supply. This is clearly true for aluminum (by a factor of 27), iron (4.1), and manganese (51) (see Table 4). The boron and sodium both appeared to decrease in the sediment. However, small changes in such small concentrations are not unexpected. The copper mass fraction was not significantly different between the sediment and cold water phases because this concentration change was small.

### Element Concentration Increases from Heating the Cold Water Supply

It is much more important from a potability aspect to consider the seven elements whose concentrations increased in the hot water. Six of these had modest increases: arsenic (11% increase), calcium (9%), lead (19%), potassium (6%), silicon (4%), and strontium

### TABLE 4. Concentrations and mass fractions of measurable elements in dried tank sediment and cold mains water supply

<table>
<thead>
<tr>
<th>Sediment a</th>
<th>EMFS b (μg·g⁻¹)</th>
<th>Main cold water supply</th>
<th>EMFS c (mg·L⁻¹)</th>
<th>EMFS d (× 1,000)</th>
<th>EMFS e (× 1,000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>Concentration</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>21,200</td>
<td>303</td>
<td>0.115</td>
<td>11.22</td>
<td>27.01</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.917</td>
<td>0.0131</td>
<td>0.000775</td>
<td>0.0756</td>
<td>0.173</td>
</tr>
<tr>
<td>Barium</td>
<td>1.28</td>
<td>0.0183</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Beryllium</td>
<td>0.18</td>
<td>0.00257</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Boron</td>
<td>36.8</td>
<td>0.526</td>
<td>0.146</td>
<td>142.5</td>
<td>0.00369</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.286</td>
<td>0.00409</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Calcium</td>
<td>526</td>
<td>7.52</td>
<td>5.62</td>
<td>485.3</td>
<td>0.0155</td>
</tr>
<tr>
<td>Chromium</td>
<td>1.85</td>
<td>0.0265</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cobalt</td>
<td>4.04</td>
<td>0.0578</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Copper</td>
<td>12,300</td>
<td>17.6</td>
<td>0.189</td>
<td>18.44</td>
<td>0.954</td>
</tr>
<tr>
<td>Gold</td>
<td>0.127</td>
<td>0.00182</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Iron</td>
<td>1,610</td>
<td>23</td>
<td>0.057</td>
<td>5.562</td>
<td>4.14</td>
</tr>
<tr>
<td>Lead</td>
<td>18.2</td>
<td>0.26</td>
<td>0.000557</td>
<td>0.03435</td>
<td>4.78</td>
</tr>
<tr>
<td>Magnesium</td>
<td>26,500</td>
<td>379</td>
<td>0.99</td>
<td>96.39</td>
<td>3.92</td>
</tr>
<tr>
<td>Manganese</td>
<td>2,100</td>
<td>30</td>
<td>0.006</td>
<td>0.5834</td>
<td>51.2</td>
</tr>
<tr>
<td>Nickel</td>
<td>14.4</td>
<td>0.206</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>245</td>
<td>3.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Potassium</td>
<td>18.5</td>
<td>0.265</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Scandium</td>
<td>0.194</td>
<td>0.00277</td>
<td>0.1</td>
<td>9.757</td>
<td>0.000284</td>
</tr>
<tr>
<td>Silicon</td>
<td>361</td>
<td>5.16</td>
<td>1.17</td>
<td>114.2</td>
<td>0.0452</td>
</tr>
<tr>
<td>Sodium</td>
<td>1,390</td>
<td>19.9</td>
<td>1.84</td>
<td>179.7</td>
<td>0.111</td>
</tr>
<tr>
<td>Strontium</td>
<td>1.18</td>
<td>0.0169</td>
<td>0.016</td>
<td>1.561</td>
<td>0.0108</td>
</tr>
<tr>
<td>Titanium</td>
<td>3.68</td>
<td>0.0526</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tungsten</td>
<td>8.19</td>
<td>0.117</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Zinc</td>
<td>3,570</td>
<td>51.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Total</td>
<td>69,911.82</td>
<td>841,35045 b</td>
<td>10.249</td>
<td>1,055,441 b</td>
<td>92.2077</td>
</tr>
<tr>
<td>Element entries</td>
<td>25</td>
<td>25</td>
<td>13</td>
<td>13</td>
<td>13</td>
</tr>
</tbody>
</table>

a Stated as the element.
b EMFS = element mass fraction in sediment (mass fraction of measurable ions in sediment).
c MFMES = mass fraction of measured elements in solute.
d EMFSCW = element mass fraction in solute of cold water.
e Used when the sediment mass fraction exceeded the solute mass fraction.
f Used when the solute mass fraction exceeded the sediment mass fraction.

*Blanks (—) denote element concentration data that were below detection limits.

*Totals differ from 1,000 because of rounding errors.
The concentration of magnesium increased by a much more substantial 151\%. Fortunately, there are no potability concentration guidelines listed for calcium, magnesium, or potassium because these have no toxicological implications. However, arsenic, iron, lead, and manganese, four elements having drinking water standards, all showed modest decreases in their potability margins: arsenic (to 8.6\% of its allowable limit in potable water), iron (17\%), lead (6.6\%), and manganese (10.8\%), but all were still well within the standards (see Table 1).

One would expect to observe a relative decrease in mass fraction in the sediment compared with the mass fraction of the solute in cold water for each of the seven elements that showed an increase in concentration in the hot water. As anticipated, decreases in the element mass fractions in the sediment were observed: arsenic (decrease 0.17), boron (0.0037), calcium (0.016), scandium (2.8 \times 10^{-4}), silicon (0.045), sodium (0.11), and strontium (0.011) (see Table 4). Magnesium, with a sediment mass fraction to cold water solute mass fraction of 4.1, was the only exception, which has been explained.

### Implications for Users

First, it should be emphasized that all of the measurable elements in both the hot and cold water samples examined were still found to be well within established potability guidelines (see Table 1). Thus the results should reassure water users that a good water supply is potable either cold or hot when the source of the water is a properly treated mains water supply feeding a regularly maintained electric water heater.

An important use of hot water in a household is to make hot drinks. This research provides some interesting features to relate to the ongoing debate as to the choice

---

**TABLE 5. Relationships between elements in dried tank sediment, cold water supply, and hot water output**

<table>
<thead>
<tr>
<th>Elements quantified</th>
<th>Concentration in dry sediment (µL(^{-1}))</th>
<th>MFDS(^b) (\times) MFCS</th>
<th>Concentration in:</th>
<th>Concentration change:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cold water (mgL(^{-1}))</td>
<td>Hot water (mgL(^{-1}))</td>
</tr>
<tr>
<td>Aluminum</td>
<td>21,200</td>
<td>184</td>
<td>0.115</td>
<td>0.085</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.917</td>
<td>1.2</td>
<td>0.775 µgL(^{-1})</td>
<td>0.857 µgL(^{-1})</td>
</tr>
<tr>
<td>Barium</td>
<td>1.28</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Beryllium</td>
<td>0.18</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Boron</td>
<td>36.8</td>
<td>0.252</td>
<td>0.146</td>
<td>0.13</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.286</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Calcium</td>
<td>526</td>
<td>0.094</td>
<td>5.62</td>
<td>6.13</td>
</tr>
<tr>
<td>Chromium</td>
<td>1.85</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cobalt</td>
<td>4.04</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Copper</td>
<td>12,300</td>
<td>65</td>
<td>0.189</td>
<td>0.118</td>
</tr>
<tr>
<td>Gold</td>
<td>0.127</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Iron</td>
<td>1610</td>
<td>28</td>
<td>0.057</td>
<td>0.051</td>
</tr>
<tr>
<td>Lead</td>
<td>18.2</td>
<td>33</td>
<td>0.557 µgL(^{-1})</td>
<td>0.665 µgL(^{-1})</td>
</tr>
<tr>
<td>Magnesium</td>
<td>26,500</td>
<td>27</td>
<td>0.99</td>
<td>2.49</td>
</tr>
<tr>
<td>Manganese</td>
<td>2,100</td>
<td>35</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>Nickel</td>
<td>14.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>245</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Potassium</td>
<td>18.5</td>
<td>0.185</td>
<td>0.1</td>
<td>0.106</td>
</tr>
<tr>
<td>Scandium</td>
<td>0.194</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Silicon</td>
<td>361</td>
<td>0.31</td>
<td>1.17</td>
<td>1.22</td>
</tr>
<tr>
<td>Sodium</td>
<td>1,390</td>
<td>0.76</td>
<td>1.84</td>
<td>1.7</td>
</tr>
<tr>
<td>Strontium</td>
<td>1.18</td>
<td>0.74</td>
<td>0.016</td>
<td>0.018</td>
</tr>
<tr>
<td>Titanium</td>
<td>3.68</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tungsten</td>
<td>8.19</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Zinc</td>
<td>3,570</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

---

\(^a\) Stated as the element for the units as given, except where otherwise stated.

\(^b\) MFDS \(\times\) MFCS = (Mass Fraction Dry Sediment) \(\times\) (Mass Fraction of Cold Solute); multiples are approximations to accommodate uncertainties in the data used.

\(^c\) Blanks (—) denote element concentrations below the detection limit of the method used for water samples. These were taken as zero for the purpose of calculating multiples.
of hot or cold water sources for their preparation. Does it matter if the hot or cold tap is used? Does it matter whether either source is boiled in an electric kettle, or a pot on the stove top element? Which option(s) minimize energy costs?

An informal survey of colleagues and friends was conducted to obtain some perspectives on the potential impact of these findings on the average water user. Almost everyone questioned chose the cold tap to fill an electric kettle, assuming the cold water quality to be higher than hot water from the water heater. Most made their choice consciously based on perceptions that there is therefore less lead (from lead/tin soldered pipe joints, etc.) in the water, or to avoid “impurities” (or “taint”) from long standing in the hot water tank as compared with standing in a cold water pipe. Some tea makers thought that the dissolved air would be higher in tea made with freshly boiled cold water, thereby improving its taste, rather than the situation with tea made from boiled hot (therefore de-aerated) water, thus giving the tea a “stewed” flavour component.

Some users were also concerned about the additional energy cost involved in filling a kettle with preheated water. Checking this out involved heating up a 5.6-m length of 1.27-cm (½-inch) inside diameter copper pipe from the hot water tank to the faucet, which would require a volume of 2.8 L for the first “hot” water to reach the faucet, and about 1½ times this volume, or 4.2 L, for the water leaving the faucet to actually be hot. So it would require twice the electricity to fill a 2-L kettle with 50°C water than it would require to heat the cold water from scratch to 50°C entirely in the kettle. It might also be slower to wait for the hot water to arrive at the tap, than to fill with cold water and switch on immediately. Of course electricity required to heat the kettle from 50 to 100°C would be the same for either scenario.

From the scenario above, filling a kettle with cold water clearly requires more time to heat it to boiling, but less energy to prepare a hot beverage than filling a kettle with hot tap water. Energy transfer on a stove between the burner and a stove top kettle is only about 80% efficient, so the use of preheated water may be defended in this application.

**A Place for Bottled Water?**

Some lapses in the availability, treatment, and potability of mains water supplies do occur temporarily, for example during planned occasional mains flushing to remove accumulated sediments or for other servicing needs of the mains supply. This is usually accompanied by an advance warning and a recommendation to residents to properly boil the affected supply before use, and store it, or to use bottled water. Occasionally a water main will suffer damage from unpredictable events, such as from construction machinery or an earthquake, with an uncertain time frame to the restoration of service. The recommended precautions under these circumstances are similar to those for programmed mains maintenance work, except that the unexpected nature of the upset makes mains water substitution by highly mobile bottled water a particularly attractive option.

A large component of the viability of marketing a bottled source of portable, potable water relies on the favourable economics of linking a low cost bottle blow moulding machine directly to a high quality, frequently analyzed water supply. The high temperature required for the blow moulding process produces a stream of inexpensive and sufficiently tough, thermally sterilized bottles which can be immediately fed to a bottling machine for filling. This simple and convenient combination of technologies continues to make bottled water a safe and affordable source of sterile water to most of those users who would either temporarily or regularly make use of this end product.

However, even bottled water is occasionally subject to contamination from various sources (Iken et al. 2002; Momani 2006). This could be microbial, from inadequately treated raw water (Nsanze et al. 1999), or from inadvertent introduction or production of a contaminant such as bromate during processing (Nyman et al. 1996). Or it could be from extraction of a harmful component from the bottle itself, especially after long storage, as found by Tamagnini and Gonzales (1997) and Croci et al. (2001). During a lapse in mains water quality, either properly boiled mains water or properly bottled (portable potable) water are appropriate for consumption by average consumers in good health (U.S. Centers for Disease Control 2006). However, for those with a weakened immune system it has been recommended that water from any source should be boiled before consumption (CRD 2008).

**Conclusions**

The heart of the results reported is from the performance of a new, fibreglass-insulated, vitreous enamel- (glass-) lined steel electric water heater. An ageing glass-lined heater would be expected to have a higher iron content in the sediment resulting from pinhole or crack access through the glass lining, which gradually exposes the steel tank shell to corrosion.

Unlined pure copper or a high copper bronze without an anode is the standard for electric hot water tank heaters in some jurisdictions. In our glass-lined tank experiments, copper showed a negligible fractional change of 0.95 in the sediment mass fraction to cold water solute mass fraction, i.e., almost neutral activity. Copper however did show a 38% decrease in concentration in the hot water stream, as compared with the cold water feed, which again would indicate a strong deposition tendency rather than a corrosive removal of copper from a copper tank.

Zinc concentrations were below detection limits in both the aqueous streams, but was present at 3.57 mg/g in the dry sediment, perhaps simply because the
concentration in the dried sediment was much higher than in the raw water. Despite the familiarity of relating corrosion resistance to the galvanizing of a more electrochemically active metal, the results from our experiments are apparently equivocal on this.

The largest observed change in element concentration in these water heater experiments was the 151% increase in magnesium concentration in the hot as compared with the cold water. This is because it is a sacrificial anode. Except for a change in the metal, one could expect a similar performance for other anode elements such as zinc.

The concentration of gold was below analytical detection limits in both the cold and hot aqueous streams, so the discovery of gold at 0.128 μg/g in the sediment was intriguing. Bearing in mind that it would take only minute traces of gold in the 20 to 25 m³ of raw water that passed through the tank in the 30-month test period to provide the measurable concentration obtained in the 6.58 g of sediment collected during this period, it is not unreasonable. This can be explained since the supply watershed is located largely in a metalliferous igneous rock basin.

A good water supply is potable, either cold or hot, when the source of the water is a properly treated mains water supply feeding a regularly maintained electric water heater. Our results are related to the characteristics of the particular supply water described. Thus a water supply containing other elements, or concentrations different from those examined here, might behave quite differently on heating. This could be an excellent opportunity for further research in other locations where there are different concentrations of suspended and dissolved solids that could affect the results.

Acknowledgments

The author thanks Tom Gore and Heather Down of the Department of Biology, University of Victoria, for photomicrographs to characterize the largely crystalline sediment particles, and Drake Hocking for a most helpful review of the manuscript. He is also grateful to survey participants for their time, and the Department of Chemistry for facilities.

References


108


Received: 16 July 2009; accepted: 23 December 2009.
Philip H. Jones Award

A student award is given at each regional symposium for the best oral presentation. This award was created as a memorial to the late Philip H. Jones, who was a founding and longstanding member of the CAWQ. It includes a cash prize of $200 at the closing ceremony of the symposium; a one-year membership in the CAWQ, including a subscription to the *Water Quality Research Journal of Canada*; the publication of the name of the winning student in an issue of the journal and on the CAWQ website; a certificate acknowledging his/her performance; and a formal invitation from the CAWQ president to submit his/her work for peer review and eventual publication in the *Water Quality Research Journal of Canada*.

At the 25th **EASTERN Canadian Symposium on Water Quality Research**, held October 30, 2009 in Ottawa, Ontario, the Philip H. Jones award winner was:

**Usman Khan,**
Department of Civil Engineering & Applied Mechanics
McGill University
Montreal, Quebec

for a presentation titled “Importance of hospitals as point sources of pharmaceutical releases to the environment.” Khan U, Nicell JA (2009).

At the 45th **CENTRAL Canadian Symposium on Water Quality Research**, held February 22–23, 2010 in Burlington, Ontario, the Philip H. Jones award winners were:

1) **Etienne Bordeleau**
Department of Civil Engineering
University of Ottawa
Ottawa, Ontario

for a presentation titled “Comprehensive Wastewater Treatment Plant and Sludge Pretreatment Model.” Bordeleau E, Droste RL (2010).

2) **Neema Prabhakaran Mariyamma**
University of Quebec
Institute National de Recherche Scientifique (INRS)
Quebec City, Quebec

for a presentation titled “Cloning of cry 1 and cry 4 genes from native *Bacillus thuringiensis* isolated from the Western Ghats of Kerala.” Prabhakaran Mariyamma N, Tyagi RD, Girija D (2010).

At the 11th **PACIFIC Canadian Symposium on Water Quality Research**, held May 1–5, 2010 in Whistler, British Columbia, the Philip H. Jones award winner was:

**Kerry Black**
Department of Civil Engineering, Faculty of Applied Science
University of British Columbia
Vancouver, British Columbia

INSTRUCTIONS FOR AUTHORS

MANUSCRIPT SUBMISSION

Requirements for submitting to and publishing in the WQRJC

Before Submission
Assistance with Online Submission and Peer Review Platform

ORGANIZATION OF THE MANUSCRIPT

What to Include and Order of Presentation

STYLE

Text
Spelling and Form
Headings
Citing References in Your Document
Reference List
Examples of Correct Forms of References
   General
   Internet / web citation
   In press citation
   Personal Communication
Tables
Equations
Illustrations

ACCEPTED MANUSCRIPTS

Submitting files for Accepted Manuscript
Required Illustration Formats for Accepted Manuscripts
Page Proofs
Preprint Online Publication
Immediate Open Access *** New Feature
Reprints
Managing Editor Contact Information

APPENDIX A: JOURNAL TITLE ABBREVIATIONS
APPENDIX B: MEASUREMENT UNIT ABBREVIATIONS
APPENDIX C: SPELLING

Manuscript Submission

Manuscripts in English or French that fall within the scope of the journal should be submitted in electronic format only (MS Word or Corel WordPerfect) through the online submission and peer review platform (http://www.editorialmanager.com/wqrjc/).

You will be asked to review and approve the electronic document assembled by the online software for the peer review process to verify that the document displays your work as you intended. Your manuscript will be submitted to the Journal office only when you are happy with and approve the assembled document.
Requirements for submitting to and publishing in the WQRJC

The following are points that you will be asked to respond to during the submission process for the Water Quality Research Journal of Canada (WQRJC):

1. The submission of this article implies that the work described has not been published previously (exceptions being in the form of an abstract or as part of a published lecture or academic thesis).
2. This article is not under consideration for publication elsewhere; if accepted, it will not be published elsewhere in the same form, in English or in any other language, without the written consent of the Publisher.
3. This publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out.
4. The references in this document are checked and verified.

Each manuscript is normally evaluated by two anonymous referees and an Associate Editor before final evaluation by the Editor. Upon final acceptance, the manuscript must be submitted in an electronic format (through the online submission system, or by email or on a disk in MS Word or Corel WordPerfect format) together with one hard copy as arranged with the Managing Editor.

Before Submission

- Authors should ensure that their manuscripts are concise, well-written, and free of typographical, grammatical, and stylistic errors. To help your manuscript move through the peer review system, consider having your manuscript proofread/edited by an editor whose first language is the same as the language in which your manuscript is written, or who has appropriate working experience in the language and in the field of study.
- Manuscripts submitted in French must also include an English translation of the title, abstract and key words.
- Manuscript Classifications: During the online submission process, you will be asked to choose classifications for your manuscript. This is one method we use to help us match your manuscript to appropriate reviewers.
- References: An accurate list of references is an essential part of a peer-reviewed, scientific article. These references may be used as resources by readers, and they are added to citation databases. Every reference mentioned in the text, tables or figures must be given in the References section, and vice versa. It is the responsibility of the authors to ensure that the details given in the References list are accurate, and as noted above, authors must verify upon submission that references have been checked and verified.

Assistance with Online Submission and Peer Review Platform

If you have difficulties using the online system, please contact the Managing Editor for assistance:

Tel.: 905-336-4513
E-mail: managing-editor@cawq.ca.

Organization of the Manuscript

What to Include and Order of Presentation

- Total number of words, including text, tables, figures, and references;
- Title of paper;
- Abbreviated title for use as a running headline (50 characters and spaces maximum);
- Full names of the authors (with the corresponding author in bold);
- Addresses of the authors including email address and contact information of corresponding author;
- Alternate Contact – coauthor information for contact in the event that you are unavailable at any time for correspondence on your manuscript from submission to publication;
- Abstract (one paragraph, 50 to 200 words in length);
- 4 to 6 key words separated by semicolons;
- The manuscript text;
- Acknowledgments (if any);
- References – Use the word “References” as the heading; see below for details;
Style

Text

Required for Submission:
- In MS Word or Corel WordPerfect format – PDF is not an acceptable form for submission;
- Length: Articles should be approximately 6000 to 8000 words in length (note: maximum length is 8000 words including text, tables, figures and references);
- Double-spaced;
- Font: 12-point size font, Times New Roman;
- Serial commas: With the exception of the final item, when three or more items are listed together in a series and are connected between the last two items by “and” or “or,” a comma should follow each word, phrase, or clause in the series; in other words, a comma should be placed after the item just before the conjunction;
- Spacing between sentences: one;
- Do not add line numbers; line numbers will be added automatically by the online submission software.

Spelling and Form

Our authority for spelling is the Webster’s Ninth New Collegiate Dictionary and the Academic Press Dictionary of Science and Technology. The Council of Biology Editors Style Manual (5th ed.) is used as the authority in matters of form.

Headings

Two styles are used in our Headings:
1) Headline style: Capitalize the first letter of the first and last words and all interior words except for articles (a, an, the), coordinate conjunctions (and, but, or, for, nor), prepositions less than 5 letters, and terms that begin with a lowercase letter (e.g., pH, Fundulus heteroclitus). These rules also apply to hyphenated terms.
2) Sentence style: Capitalize the first word of the heading and those words that would be capitalized within regular text (proper nouns and adjectives).

For illustration, the following heading descriptions are portrayed in their corresponding style:

First-Order Headings

First-order headings (e.g., Introduction, Materials and Methods, Results, etc.) should be centred, bold, and in headline style with a space above and below.

Second-Order Headings

Second-order headings should be flush left, bold, and in headline style with a space above and below.

Third-order headings. Third-order headings should be flush left, italicized, bold, in sentence style capitalization, inline with the following text, end with a period, and have one space above.

Citing References in Your Document

- The author-date system of reference citation should be used in the text.
- No punctuation is used between author and date.
- Use “et al.” for more than two authors. Do not italicize “et al.”
Multiple citations in one parenthetical citation are separated by semicolons and arranged chronologically, and then, if necessary, alphabetically: e.g., Smith 1993; Jones 2000; Munch and Carter 2000; Roberts et al. 2003.

**Reference List**

- The heading for your list should be “References.”
- The list of references should be arranged alphabetically by author, and chronologically for each author if necessary.
- Each reference should have a hanging indent of five spaces.

**Authors’ names.** Use surname followed by initials in boldface type for every author, separated by commas. There are no periods after initials (see examples below).

**Year of publication.** Put a period after the year.

**Article title.** Use sentence capitalization in article titles; i.e., capitalize the first letter of the first word. Capitalize the first letter of the first word of a subtitle if it follows a period but not if it follows a colon, dash, or other mark of punctuation.

**Journal title.** Follow guidelines in the *World List of Scientific Periodicals* for abbreviations of journal titles (see also Appendix A for selected journal title abbreviations).

**Volume and page numbers.** The volume number of a journal is set in boldface type, followed by a boldface colon. Page numbers are given in full (200–225), joined by an en dash (for en dash, use Alt + 0150), closed up to the colon, and followed by a period.

**Chapter of a published book.** Follow the form used for journal articles for authors’ names and year of publication. Treat the title like the title of a journal article, but follow it with a comma, and the page numbers (abbreviated p., not pp.), joined by an en dash and followed by a period. Editors’ names are preceded by “In.” The names are followed by “(ed.),” a comma, and the title of the book. Use sentence capitalization for book titles. The names of conferences and official bodies have every important word capitalized.

**Examples of Correct Forms of References**

**General**


**Internet / web citation**

In press citation


- Cite in text as: (Culp et al. In press).

Personal Communication

- Cite in text as: (Culp personal comm. 2002).

Tables

- All tables should be referred to by number in the text (e.g., ... presented in Table 1);
- The table number and caption should appear at the top of the table aligned against the left margin with ‘table’ in capital letters and only the first letter of the first word of caption capitalized (e.g., TABLE 1. Chemical composition of lake water);
- A table caption must be a noun phrase, not a complete sentence, and there is no period at the end. Delete explanatory notes that involve complete sentences and transfer them to a footnote. Table footnotes should be indicated by superscript letters;
- Tables should be prepared on separate sheets in aligning rows and columns;
- Arrange tables with like data reading downwards; some exceptions allowed;
- Please endeavour to create your tables from the table menu in Word or WordPerfect.

Equations

- Equations should be centred on the page and identified by a number in parentheses placed flush with the right-hand margin;
- Do not use an equation editor to insert special symbols as part of the manuscript text.

Illustrations

- All figures must be cited in the text;
- Use style of reference as (Fig. 1) or Fig. 1 within sentence; use Figure 1 to start a sentence;
- The figures and the list of figure captions should be separate from the main text;
- Bear in mind, when preparing illustrations, that they will be reduced to fit within the width of a journal column (approximately 8 cm) or page (approximately 17 cm);
- In bar graphs, use patterns instead of varying degrees of shading for clearer definition; do not use colour;
- If colour figures (e.g., photographs) are submitted and accepted, and the author(s) wishes to have the colour version published, the full cost of scanning (if necessary) and printing may need to be borne by the author.

Accepted Manuscripts

Submitting files for Accepted Manuscript

Upon final acceptance, the manuscript must be submitted in an electronic format (through the online submission system, or by email or on a disk in Word or WordPerfect format) together with one hard copy (or other acceptable format) as arranged with the Managing Editor.

Required Illustration Formats for Accepted Manuscripts

- Electronic graphic files must be submitted as:
  - TIFF files (photos) at 300 dpi, or
  - EPS files (line art: graphs, technical art, etc.) at 600 dpi;
- Electronic graphic files must be provided at approximately the size they will be placed (usually about 8 cm in width). Graphic files in these formats can be from original art created at the above resolution or scanned at the above resolution;
- Authors must ensure that numbers and letters on illustrations are large enough to be fully legible;
Authors are also requested to ensure that tones in computer-generated illustrations contrast sufficiently and that very bright tones are not so light that they disappear in print. *PowerPoint presentation files and graphics embedded in word processing or spreadsheet documents are not acceptable.*

If it is not possible to submit electronic graphic files as per the instructions above, originals (not photocopies) should be submitted in black and white. *A scanning cost of $15 per illustration will be borne by the author.*

Beginning with the first issue of 2010, we are printing qualifying figures in colour at no additional cost to authors.

**NOTE:** this is subject to change without notice and it is possible we will revert to the author paying in full for the additional cost associated with colour printing. For more information, contact the Managing Editor directly.

**Page Proofs**

Copyediting is performed by the Managing Editor. One set of page proofs is sent to the principal author to be checked before publication. The proof stage is not the time to make extensive corrections. Changes must be limited to correction of spelling errors, incorrect data, and updated information for “submitted” and “in press” references.

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To allow for timely exposure of accepted manuscripts and with Author permission, we post papers online that are ready for printing before the entire issue is ready for publication. These papers may or may not have page numbers added, can be found in our latest “Current Issue,” and are accessible in full to all members of the CAWQ; the abstracts can be viewed by anyone. Once all manuscripts for an issue are complete, any missing page numbers will be added and the issue will be finalized. As soon as the first paper for the next issue is ready, a new “Current Issue” will be started.

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We now offer the option to have immediate Open Access to articles for anyone interested in viewing the content.

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*Water Quality Research Journal of Canada*  
Canada Centre for Inland Waters  
867 Lakeshore Road  
Burlington, Ontario  
Canada L7R 4A6
### APPENDIX A

**Water Quality Research Journal of Canada**

**Selected Journal Title Abbreviations**

<table>
<thead>
<tr>
<th>Journal Title Abbreviations</th>
</tr>
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<tbody>
<tr>
<td>Agric. For. Meteorol.</td>
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### APPENDIX A - Continued
Water Quality Research Journal of Canada
Selected Journal Title Abbreviations

<table>
<thead>
<tr>
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<th>Full Journal Title</th>
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<td>Mon. Weather Rev.</td>
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<td>Toxicology</td>
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<td>Waste Manage.</td>
<td>Water Environment Research</td>
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<td>Water, Air, Soil Pollut.</td>
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### APPENDIX B
Water Quality Research Journal of Canada
Measurement Unit Abbreviations

<table>
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<td>centimetre</td>
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<td>mole</td>
<td>mol</td>
</tr>
<tr>
<td>hertz</td>
<td>Hz</td>
<td>newton</td>
<td>N</td>
</tr>
<tr>
<td>kilo</td>
<td>k</td>
<td>ounce</td>
<td>oz</td>
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<td>kelvin</td>
<td>K</td>
<td>pascal</td>
<td>Pa</td>
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<tr>
<td>kilogram</td>
<td>kg</td>
<td>second</td>
<td>s</td>
</tr>
<tr>
<td>litre</td>
<td>L</td>
<td>temperature</td>
<td>temp (tables only)</td>
</tr>
<tr>
<td>metre</td>
<td>m</td>
<td>tonne</td>
<td>t (tables only)</td>
</tr>
<tr>
<td>micro</td>
<td>μ</td>
<td>volume</td>
<td>vol (tables only)</td>
</tr>
<tr>
<td>microgram</td>
<td>μg</td>
<td>week</td>
<td>wk (tables only)</td>
</tr>
<tr>
<td>milligram</td>
<td>mg</td>
<td>year</td>
<td>yr (tables only)</td>
</tr>
</tbody>
</table>
APPENDIX C
Water Quality Research Journal of Canada
Spelling

The following words are frequently encountered in the Water Quality Research Journal of Canada manuscripts. Please adhere to the following spelling.

acknowledgment
airborne
alga (s.), algae (pl.)
alogous
baseline (always solid)
bioassay
analyze
blue-green algae
brewer’s yeast
buildup (n.) build up (v.)
by-product
cannot
chloro-organic
chlorophyll a, b
cleanup (n.), clean up (v.)
coauthor
coopertion
data (plural)
database
decision making
decision-making process (add hyphen when used adjectively)
dec-ice(r)
desiccate
die-off
det al. (not italicized)
fiberglass
flowthrough
focused, focusing
food web
fresh water (n.), freshwater (adj.)
groundwater

half-life
inasmuch as
in-house (always hyphenated)
in situ, in vivo, in vitro—roman
instream
jar test
Julian day
least-squares method (hyphen as adj.)
microorganism
modelling
ongoing
onshore
offshore
physicochemical
percent
phosphorus (n.), phosphorous (adj.)
pre (prefix), always solid, even with double vowels
preexposure
Pyrex
snowmelt
stormwater
Student’s t test
runoff
seawater
Secchi depth
sulfate, sulfide, sulfur
ultraviolet
U.S. EPA
versus—not vs, except in tables
wastewater
wavelength
DIRECTIVES AUX AUTEURS

SOUMISSION DES MANUSCRITS

EXIGENCES POUR LA SOUMISSION ET LA PUBLICATION DANS LE WQRJC

Avant d’expédier leur manuscrit
Aide avec la présentation en ligne et le système de révision par les pairs

ORGANISATION DU MANUSCRIPT

Ce qu’il faut inclure et ordre de la présentation

STYLE

Texte
Orthographe
Titres
Citations de références dans le texte
Liste de références
Exemples de références
Général
Citation Internet
Citation « sous presse »
Communication personnelle
Tableaux
Équations
Illustrations

MANUSCRITS ACCEPTÉS

Soumission des fichiers d’un manuscrit accepté
Format d’illustration requis pour les manuscrits acceptés
Épreuves et tirés à part
Préimpression de la publication en ligne
Réimpressions
Directeur de la rédaction coordonnées

Soumission des manuscrits

Les auteurs dont le manuscrit, anglais ou français, correspond à l’orientation de la revue devraient présenter leur manuscrit en format électronique (Word ou WordPerfect) avec la présentation en ligne et le système de révision par les pairs (http://www.editorialmanager.com/wqrjc/).

On vous demandera d’évaluer et d’approuver le document électronique assemblé par le logiciel en ligne pour le processus de révision des pairs afin de vérifier que le logiciel présente votre travail comme il se doit. Votre manuscrit sera soumis au bureau du Journal seulement lorsque vous serez satisfait du document assemblé et que vous l’aurez approuvé.
Exigences pour la soumission et la publication dans le WQRJC

Vous devez satisfaire aux exigences suivantes pour le processus de soumission pour le Water Quality Research Journal of Canada (WQRJC):

1. La présentation de cet article signifie que le travail décrit n’a pas déjà été publié (sauf sous forme d’extrait ou en tant que partie d’une conférence publiée ou d’une thèse universitaire).
2. Cet article n’est pas à l’étude pour une autre publication et s’il est accepté, il ne sera pas publié ailleurs sous la même forme, en anglais ou dans une autre langue, sans le consentement écrit de l’éditeur.
3. Cette publication est approuvée par tous les auteurs et a obtenu le consentement tacite et explicite des autorités responsables où le travail a été effectué.
4. La liste des lectures de référence comprise dans ce document est exacte et toutes les références ont été revérifiées pour en assurer l’exactitude.

Normalement, tous les manuscrits sont évalués par deux réviseurs anonymes et un rédacteur en chef adjoint avant d’être transmis au rédacteur en chef pour évaluation finale. Une fois approuvés, les manuscrits doivent être présentés en format électronique (par l’entremise du système de présentation en ligne, par courriel ou sur une disquette en format MS Word ou Corel WordPerfect) et en copie papier, comme cela a été convenu avec le directeur de la rédaction.

Avant d’expédier leur manuscrit

- Les auteurs devraient s’assurer qu’il est concis, bien rédigé et exempt d’erreurs typographiques, grammaticales et stylistiques. Pour que votre manuscrit passe d’une étape à l’autre du système de révision par les pairs plus rapidement, vous pouvez faire corriger/réviser votre manuscrit par un réviseur dont la langue maternelle est la même que celle de votre manuscrit, ou qui a une expérience de travail reconnue dans la langue et le champ d’étude de l’article.
- Tout manuscrit français doit également être accompagné d’une version anglaise du titre, du résumé et des mots clés.
- Classifications du manuscrit : Durant le processus de présentation en ligne, on vous demandera de choisir une catégorie pour votre manuscrit. Il s’agit d’une méthode que nous utilisons afin de nous aider à jumeler votre manuscrit aux bons examinateurs.
- Références : Une liste à jour des sources est une section essentielle d’un article scientifique révisé par des pairs. De telles références peuvent servir aux lecteurs et elles sont intégrées à la base de données des sources. Toute source citée dans le corps de l’article, les tableaux ou les figures doit figurer dans les références et vice versa. Il incombe aux auteurs de vérifier que les détails donnés dans la liste des sources sont exacts, et comme cela est mentionné ci-dessus, les auteurs doivent s’assurer au moment de la présentation que les références ont été vérifiées.

Aide avec la présentation en ligne et le système de révision par les pairs

Si vous rencontrez des difficultés avec l’utilisation du système en ligne, prière de communiquer avec le directeur de la rédaction.

Téléphone : 905-336-4513;
Courrier électronique : managing-editor@cawq.ca.

Organisation du manuscript

Ce qu’il faut inclure et ordre de la présentation

- Nombre total de mots, en incluant le texte, les tableaux, les figures et les références;
- Le titre de l’article ;
- Un titre courant ; pour l’utiliser comme titre courant (50 caractères et espaces maximum);
- Les noms complets des auteurs (et le nom de l’auteur correspondant en gras) ;
- Les adresses des auteurs (y compris l’adresse courriel et les coordonnées de l’auteur correspondant) ;
• Autre personne-ressource – renseignements du coauteur si vous n’êtes pas disponible à n’importe quel moment du processus de soumission de votre manuscrit pour publication.
• Le résumé (un paragraphe de 50 à 200 mots) ;
• Quatre à six mots clés (séparés par des points-virgules) ;
• Le texte ;
• Les remerciements (le cas échéant);
• Les références ;
• Liste de symboles ou d’acronymes utilisés (si 15 ou plus);
• Les tableaux ;
• les légendes des figures (page séparée) ;
• Chaque page du manuscrit doit être numérotée ;
• Figures et illustrations – Fichiers séparés pour chaque figure ou illustration OU des figures ou illustrations joints à la fin du fichier manuscrit (pour la présentation seulement); pour lire les instructions cliquez sur Formats exigés pour les illustrations des manuscrits acceptés

Style

Texte

Exigences pour la soumission
• En format MS Word ou Corel WordPerfect – Le PDF n’est pas un format accepté pour la présentation
• Nombre de mots : En général, les manuscrits doivent comprendre de 6,000 à 8,000 mots (Note : 8 000 mots maximum, en incluant le texte, les tableaux et les références)
• Double interligne
• Police de caractères : Police de 12 points, en Times New Roman
• Série de virgules : Lorsqu’une série de trois termes ou plus sont énumérés ensemble et que les deux derniers termes sont réunis par « et » ou « ou », on devrait employer une virgule après chaque mot, chaque phrase ou proposition de la série, à l’exception du dernier terme; en d’autres mots, on devrait employer une virgule après le terme tout juste devant la conjonction;
• Espacement entre les phrases : une espace;
• Ne pas ajouter de numéros de lignes, car ces dernières seront calculées automatiquement par le logiciel de présentation en ligne

Orthographe

Le dictionnaire utilisé pour l’orthographe est Le Robert.

Titres

Les titres de sections principales (Introduction, Matériels et méthodes, Résultats, Discussion, Conclusion) doivent être centrés, avec la première lettre du premier mot en majuscule.

Les titres de sections secondaires doivent être alignés à gauche, avec la première lettre du premier mot en majuscule.

Les titres de sections tertiaires doivent être en retrait de cinq espaces. La première ligne de chaque paragraphe doit être en retrait de cinq espaces. Pour faciliter la lecture des manuscrits par nos réviseurs, veuillez les imprimer en police de caractères 12.

Citations de références dans le texte

• Les citations littéraires doivent être indiquées dans le texte selon l’auteur et la date.
• Aucune ponctuation n’est utilisée entre le nom de l’auteur et la date.
• Utiliser « et al. » s’il y a plus de deux auteurs. Ne pas mettre « et al. » en italique.
• Si plusieurs citations sont présentées entre parenthèses, elles doivent être séparées d’un point-virgule et disposées par ordre chronologique et ensuite, au besoin, en ordre alphabétique : Smith 1993; Jones 2000; Munch et Carter 2000; Roberts et al. 2003.
Liste de références

- Le titre de la liste doit être « Références ». The heading for your list should be « Références. »
- La liste de références doit être présentée dans l’ordre alphabétique, par auteur et, si nécessaire, dans l’ordre chronologique pour chaque auteur.
- Chaque référence doit avoir des alinéas en sommaire de cinq espaces.

Nom des auteurs. On utilise le nom de famille suivi des initiales pour chaque auteur. Il n’y a pas de point après les initiales (voir exemples ci-dessous).

L’année de publication. Mettre un point après l’année.

Le titre de l’article. Seulement la première lettre du premier mot doit être en lettre majuscule. Il en est de même pour la première lettre du premier mot d’un sous-titre.

Nom du périodique. Veuillez suivre les directives fournies dans l'ouvrage Word List of Scientific Periodicals. L’appendice A qui suit contient une liste d’abréviations de titres de périodiques qui sont fréquemment mentionnées dans notre revue.


Livres. Le titre du chapitre d’un livre est présenté de la même manière que le titre d’un article, excepté qu’il est suivi d’une virgule et du numéro des pages. Le mot “Dans” précède le nom de l’éditeur, lequel est suivi par une virgule, et le titre du livre.

Exemples de références

Général


Citation Internet


Citation « sous presse »

Culp JM, Podemski CL, Cash KJ. Interactive effects of nutrients and contaminates from pulp mill effluents on riverine benthos. J. Aquat. Ecosyst. Stress Recovery, sous presse

Cite in text as: (Culp et al. sous presse)
Communication personnelle

- Citer dans le texte de la manière suivante : (Culp comm. personnelle. 2002).

Tableaux

- On doit référer aux tableaux dans le texte par leur numéro.
- Le numéro et le titre du tableau doivent apparaître au-dessus du tableau, alignés contre la marge de gauche avec seulement la première lettre du premier mot en majuscule.
- Le titre du tableau est un syntagme nominal et il n’y a pas de point à la fin. Si des notes explicatives sont nécessaires, présentez-les sous forme de renvois avec des chiffres en indice supérieur. Les notes de bas de page des tableaux devraient être présentées sous forme de renvois au bas du tableau avec des chiffres en indice supérieur.
- Les tableaux doivent être présentés sur des feuilles individuelles.
- Disposez les tableaux de façon à lire les données vers le bas. Toutefois, certaines exceptions sont permises
- Si possible, utilisez le menu des tableaux offert par Word ou WordPerfect.

Équations

- Les équations doivent être centrées par rapport à la page; elles doivent être identifiées par un numéro placé entre parenthèses contre la marge de droite.
- N’utilisez pas d’éditeur d’équations afin d’insérer des symboles spéciaux dans le manuscrit.

Illustrations

- Toutes les illustrations doivent être citées dans le texte.
- La liste des figures doit être séparée du texte.
- On doit tenir compte du fait que toutes les illustrations devront être réduites pour cadrer avec la largeur d’une colonne (8 cm) ou une page (17 cm) de la revue.
- Pour les graphiques en barre, veuillez vous servir de symboles au lieu de différentes nuances d’ombres afin d’obtenir une définition mieux marquée.
- Si des figures en couleur (p. ex. : photographie) sont présentées et acceptées, et que l’auteur ou les auteurs désirent publier la version couleur, le coût total de la numérisation (au besoin) et de l’impression sera assumé par l’auteur ou les auteurs.

Manuscrits acceptés

Soumission des fichiers d’un manuscrit accepté

Une fois approuvé, le manuscrit devra être présenté en format électronique (par l’entremise du système de présentation en ligne, par courriel ou sur une disquette en format Word ou WordPerfect) et en copie papier (ou un autre format autorisé) tel cela a été convenu avec le directeur de la rédaction.

Format d’illustration requis pour les manuscrits acceptés

- Les fichiers graphiques électroniques doivent être soumis sous forme de fichiers :
  - TIFF (photos) à 300 dpi, ou de fichiers
  - EPS (dessin au trait : graphiques, art technique, etc.) à 600 dpi,
- Les fichiers électroniques doivent être fournis approximativement à la taille à laquelle ils seront utilisés (habituellement environ 8 cm de largeur). Les fichiers graphiques dans ces formats peuvent provenir d’un original créé à la résolution ci-dessus ou avoir été numérisés à la résolution ci-dessus.
Les auteurs doivent veiller à ce que les numéros et les lettres des illustrations soient assez larges pour être entièrement lisibles.

Les auteurs doivent également s’assurer que les tons des illustrations générées par ordinateurs aient suffisamment de contraste et que les tons très clairs ne soient pas légers de sorte qu’ils disparaissent à l’impression. Les fichiers et les graphiques de présentation PowerPoint intercalés dans les documents de traitement de texte et les tableurs ne peuvent pas être acceptés.

S’il n’est pas possible de présenter des fichiers graphiques électroniques conformément aux instructions qui précèdent, il faut présenter des originaux (pas des photocopies) en noir et blanc. Des frais de numérisation de 15 $ par illustration seront facturés à l’auteur.

Si des figures en couleur sont présentées et acceptées, et que l’auteur ou les auteurs désirent avoir la version couleur plutôt qu’en gamme de gris, le coût total de la numérisation (au besoin) et de l’impression sera assumé par l’auteur.

Épreuves et tirés à part

Les épreuves seront envoyées à l’auteur principal pour vérification. À l’étape des épreuves, on ne doit pas apporter des corrections majeures au manuscrit. Les changements doivent se limiter à la correction d’erreurs d’orthographe, de données erronées ou d’erreurs grammaticales ainsi qu’à la mise à jour des références “soumises” ou “sous presse”.

Préimpression de la publication en ligne

Pour exposer en temps opportun les manuscrits acceptés, nous affichons en ligne, avec l’autorisation de l’auteur, les articles qui sont prêts à être imprimés avant que le numéro au complet soit prêt à être publié. Ces articles, qui peuvent ou non être paginés, se trouvent dans notre plus récent «article disponible» et sont entièrement accessibles à tous les membres de l’ACQE; les résumés peuvent être consultés par tout le monde. Une fois que tous les manuscrits d’un numéro sont terminés, tous les numéros de page qui manquent seront ajoutés et le numéro sera finalisé. Aussitôt que le premier article du prochain numéro est prêt, un nouvel «article disponible» sera commencé.

Réimpressions

Tous les auteurs reçoivent une copie gratuite en format PDF de leur document.

Directeur de la rédaction coordonnées

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Fax: 905-336-4420
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867 chemin Lakeshore
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Canada L7R 4A6
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