MEMORIAL UNIVERSITY

THE HARRIS CENTRE Memorial University

Linking organic matter source to disinfection byproduct formation in drinking water supplies

Susan Ziegler, Department of Earth Sciences, Memorial University

Applied Research Fund 2008-2009

This research project was funded under the Harris Centre's Applied Research Fund. The intellectual property vests with the author(s). For more information about the Applied Research Fund or to obtain hard copies of this report, please contact the Harris Centre.

Linking organic matter source to disinfection byproduct formation in drinking water supplies

Susan Ziegler, PI
Susan Hannan, graduate student

This research project is focused on determining how the sources of organic matter in water supplies is related to the generation of disinfection byproducts (DBPs) when chlorinated during treatment. This is truly a long-term project, however, through the funding from the Harris Centre's Applied Research Fund we have been able to address the three original goals outlined in the original proposal aimed at developing key hypotheses to address the problem of elevated DBPs in many drinking water supplies in the province.

1. Analysis of Provincial Dataset:
Provincial data on chlorinated disinfection byproducts (CDBPs) across the province was analyzed against watershed composition and water quality parameters. These analyses provided some insight into the potential role of dissolved organic matter source in regulating the yield of CDBPs. We found that watersheds with considerably more deciduous forest cover tended to have higher levels of CDBPs, however, such relationships were not statistically significant. This analysis also clearly indicated that pH, dissolved organic carbon (DOC), and color were not important predictors for CDBP yields in drinking water. This initial investigation of existing provincial data confirmed similar results that have been reported in the most recent report entitled "Best management practices for the control of disinfection by-products in drinking water systems in Newfoundland and Labrador completed by the Water Resources Division in April 2009.

Results from our analyses of the existing provincial data and review of the most current Water Resources report has been used to direct a current investigation using the newest available data (April 2009) which includes both trihalomethanes and haloacetic acids. This analysis is currently being carried out by Susan Hannan. She began this work in September 2009, following a meeting we had with Paula Dawe and Annette Dobin from the Water Resources Division. We anticipate using the results of this analysis to inform our next steps aimed at coupling our laboratory chlorination experiments with samples collected from targeted water supplies across the province.

2. Controlled Chlorination Experiments Using Range of Provincial Water Sources:
A series of controlled chlorination experiments using a range of targeted drinking water sources were conducted as a result of our analysis and review of the provincial database on DBPs which indicated that controlled experimentation was necessary. The water supplies sampled were chosen both on the basis of CDBP concentrations in the treated water and on watershed composition. The results here are based upon controlled chlorination and as such have removed one major confounding factor we ran into while analyzing the provincial data set; The current data is based upon treated drinking water rather then the source water itself. Therefore, DBP levels reported by Water Resources (and any monitoring organization for drinking water) is a result of the combined effects of water source, treatment process, and distribution. Conducting controlled chlorination experiments has allowed us to make direct comparisons among water sources to investigate the water quality attributes that may regulate DBP yields in drinking water.

We found that higher yields of specific groups of CDBPs and specific individual CDBPs were significantly related to some watershed vegetation composition. Total trihalomethane concentrations, which are currently monitored by the provincial government, were correlated with percent cover of tall shrubs (likely dominated by alder) and dense deciduous (Fig. 1). This

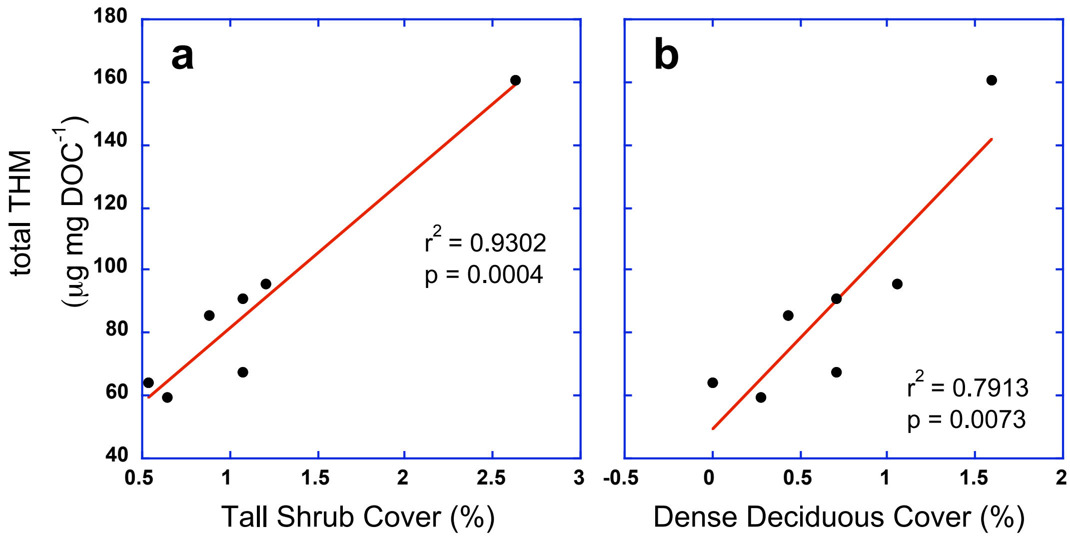

Figure 1. Least squares linear regression results for total trihalomethane (THM) yields, normalized to dissolved organic carbon (DOC) concentrations, from drinking supply water samples collected and chlorinated under controlled experimental conductions versus tall shrub (a) and dense deciduous cover (b) as a percent of the total watershed area. The drinking water supplies were all located in on the Avalon peninsula and represented a large range in THM levels as reported by the NL Provincial Government.

suggests that deciduous vegetation cover in a watershed may in some way control the yield of THM in treated drinking water. Although there could be a number of explanations for this correlation, one probable explanation is that deciduous litter and the soils derived from deciduous litter contribute great proportions of DBP precursors to the dissolved organic matter (DOM) found in surface waters including drinking water supplies such as those tested here (REF). Further the data suggest that increased watershed deciduous forest cover and deciduous shrub is correlated to increased yields of specific DBPs such as chloropirin, chlorodibromomethane, bromoform, dibromoacetonitrile (Table 1.; Fig. 2a). On the other hand, greater watershed coniferous forest cover appears to be negatively correlated with DBP yield including bromodichloromethane and chlorodibromomethane (Fig. 2b; Table 1). This negative correlation likely reflects some co-correlation with some other factor such as coverage by another watershed cover type that contributes more to DBP precursors relative to coniferous forest inputs. Wetland sources of DOM are often investigated due to their higher yield of hydrophobic DOM which may participate in the formation of DBP relative to hydrophilic DOM components. Here we found that wetland cover as a percent of the total watershed area was

Table 1. The least squares regression analyses results for ten individual or class of disinfection byproducts (DBP; normalized to dissolved organic carbon concentration in mg C L^{-1}) that exhibited significant correlations ($\alpha = 0.05$) with some watershed cover type expressed as a percent of total watershed area. The + and – signs signify whether the correlation was positive or negative. Cover type as a percent was based upon the Forestry Inventory Database from 2001, analyzed using GIS software and provided by the Water Resources Division, NL Department of Environment and Conservation.

Analyte	Cover Type (%)	R^2	p-value	+ or -
TTHM	Tall Shrub	0.93	0.0004	+
Chloroform	Tall Shrub	0.93	0.0005	+
Chlorodibromomethane	Herbs	0.88	0.002	+
Dibromoacetonitrile	Sparse Deciduous	0.88	0.002	+
Dibromoacetonitrile	Low Shrub	0.86	0.002	+
Chloropicrin	Forest	0.84	0.003	-
Dibromoacetonitrile	Non-forest Vegetation	0.84	0.003	+
Chloropicrin	Sparse Deciduous	0.84	0.004	+
Chlorodibromomethane	Dense Coniferous	0.82	0.005	-
Chloropicrin	Herbs	0.82	0.005	+

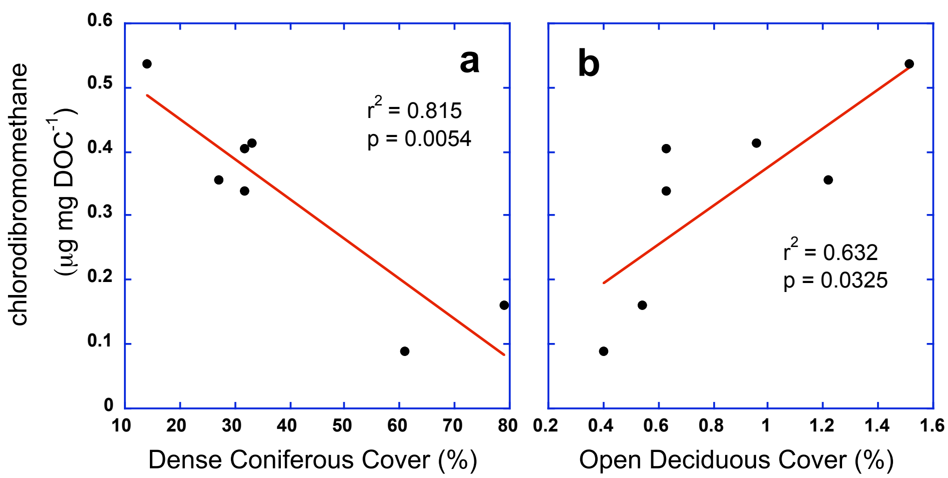

Figure 2. Least squares linear regression results for total chlorodibromomethane yields, normalized to dissolved organic carbon (DOC) concentrations, from drinking supply water samples collected and chlorinated under controlled experimental conductions versus dense coniferous forest cover (a) and open deciduous cover (b) as a percent of the total watershed area. The drinking water supplies were all located in on the Avalon peninsula and represented a large range in THM levels as reported by the NL Provincial Government.

positively correlated with bromoform and dibromoacetonitrile (Fig. 3). These relationships, however, are dependent upon one water source that had a high percent wetland cover but are supported by significant positive correlations between bromoform, dibromoacetonitrile and wetland shrub and wetland herb cover as a percent of total watershed area (Fig. 4).

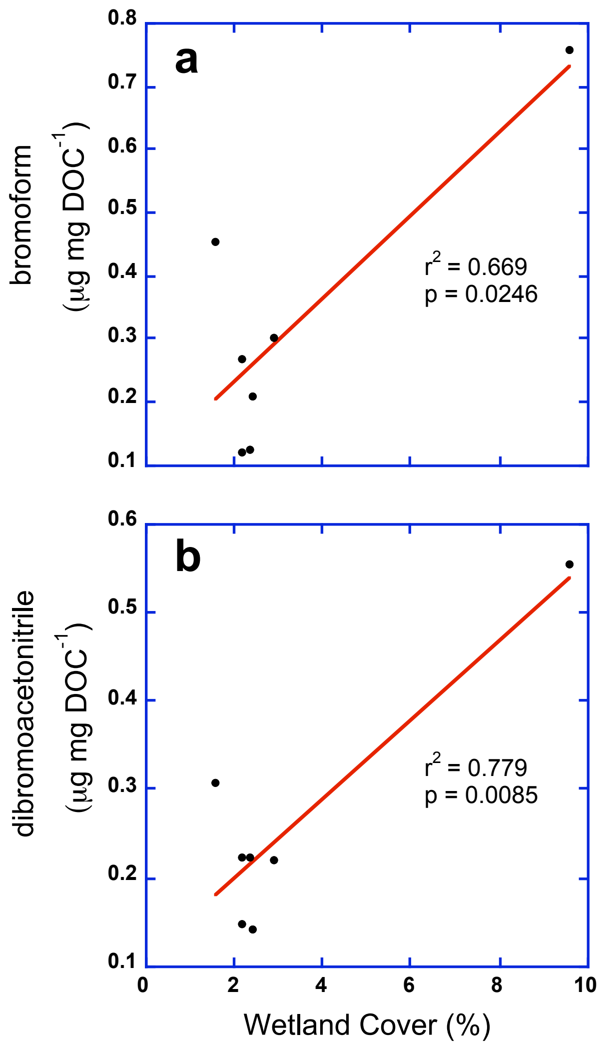

Figure 3. Least squares linear regression results for total bromoform (a) and dibromoacetonitrile yields, normalized to dissolved organic carbon (DOC) concentrations, from drinking supply water samples collected and chlorinated under controlled experimental conductions versus total wetland cover as a percent of the total watershed area. The drinking water supplies were all located in on the Avalon peninsula and represented a large range in THM levels as reported by the NL Provincial Government.

The results of these controlled chlorinations are intriguing because correlations with specific DBP appear to be more numerous then with total THM yield suggesting the need to investigate specific contaminants in order to determine how watershed composition may regulate yield of DBPs in addition to determining techniques to reduce to formation of these from existing water supplies. It is important to point out, however, that the relationships we investigated here between the CDBP yield and watershed vegetation are simply correlative and not a direct indicator of the role of organic matter source in predicting CDBP yield. The results of these analyses into the research proposal Susan Hannan presented to her thesis advisory committee in the 2009. This proposal outlines a series of experiments to test the DBP formation potential of specific watershed sources of DOM discussed below.

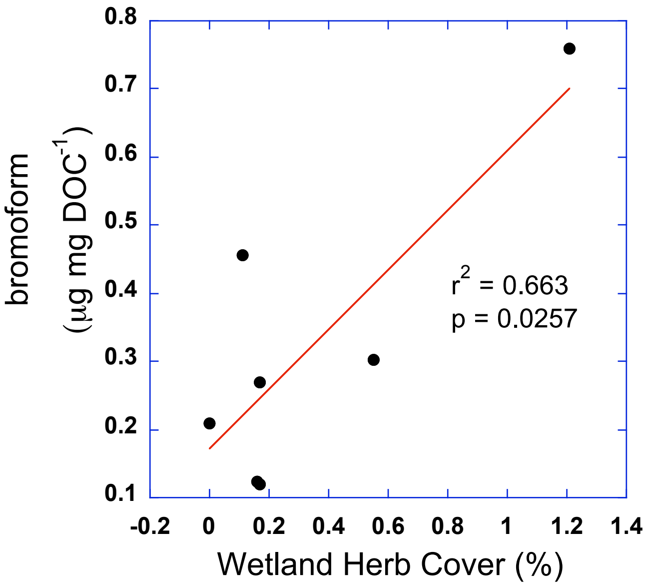

Figure 4. Least squares linear regression results for total bromoform, normalized to dissolved organic carbon (DOC) concentrations, from drinking supply water samples collected and chlorinated under controlled experimental conductions versus total wetland herb cover as a percent of the total watershed area. The drinking water supplies were all located in on the Avalon peninsula and represented a large range in THM levels as reported by the NL Provincial Government.

3. Chlorination Experiments Using Key Watershed Organic Matter Sources:
There has been some delay in progress with regard to the completion of the chlorination experiments using watershed organic matter sources. This has been in part due to a combination of change in personnel working on this project and instrumentation problems. Sheldon Huelin, who began work on this project upon its inception, decided not to pursue further graduate studies at this time and remains in his current position at MUN. Sheldon, had been awarded a Aldrich Fellowship based upon his application to do a Ph.D in Environmental Sciences including his proposal to continue the work he began on this project. Due to personal reasons, Sheldon, decided not to take up the opportunity although he remains in touch due to interest in the project. Susan Hannan, an Environmental Science MSc student, was interested in picking up this project and began her programmer here at MUN September 1, 2008. She is currently working with a series of organic matter sources collected from watersheds on the Avalon Pennisula. The location and collection of these sources was based upon the results of our previous experiments described above and represent sources we suspect may yield differences in DBP formation and are likely important sources of DOM in water supplies in this region. Susan has completed the generation of DOM samples from two types of deciduous litter, two types of coniferous litter, sphagnum moss litter, and the soils associated with these litter sources. These DOM samples will be used in a series of chlorination and photochemical experiments to determine how such sources regulate CDBP yields and what role UV treatment (photochemical) of such sources has in reducing the precursors for these contaminants.

To accomplish this goal Ms. Hannan completed a proposal outlining these experiments. Following review of the experimental plan by her committee, in February 2009, Susan completed the entire suite of key organic matter source leachates for her experiments. Since that time she has analyzed all of these samples for dissolved organic carbon, total dissolved nitrogen, chloride, nitrate, sulfate, absorbance and spectral slope, and will be completing the chlorine demand ammonium and phosphate analysis this winter.

Ms. Hannan has also establish the methods, obtained the appropriate surrogates and standards for the haloacetic acid method. This required review of the literature and determination of the best approach for the type of samples we will be working with. These preparations now make it possible for her to set up both trihalomethane and haloacetic acid analyses by gas chromatography (GC) with an electro capture detector (ECD; the same system used to complete our THM analyses). Unfortunately we have run into problems with this GC-ECD system and Susan herself has been working at each component of this GC-ECD system to get it up and running. This has been a very slow process given the common use nature of this instrument housed in a common laboratory in the engineering building. It was our goal to have completed a set of standard tests for both THM and HAAs on this system this past summer so that Susan could begin her next chlorination experiments using the leachates prepared before the end of September. The issues have arisen due to computer failure and communication errors following the installation of a different computer and new software during the interim between when Sheldon Huelin finished his work and Susan began her testing this year. We have recently determined that the newly purchased interface card is faulty and will be replaced before the first week of December.

Further, to obtain her anion concentrations Susan had to work on the ion chromatographic system to optimize the analysis due to problems with that instrument which was also brought out of decommissioning for the purpose of these analyses. This was successful and so we are now poised to continue future work using this system, however, it cost more time then originally anticipated for this project.

Results from this project and the ongoing work stemming from this project have lead to a new collaboration with the Water Resources Division of the NL Department of Environment. Through meetings with Paula Dawe and Annette Dobin we have formed a list of common research goals which stem from the research supported by this ARF grant. Annette Dobin is now on Susan Hannan's advisory committee and we have applied for support from the Institute for Biodiversity and Ecosystem Science and Sustainability to support a related aspect of this research. The main objectives of the research stemming from this project are to:

I. Complete a set of controlled chlorination experiments to determine the trihalomethane (THM) and haloacetic acid (HAA) formation potential of specific chemical fractions of key watershed DOM sources following our analysis of results from bulk source materials.

II. Establish whether chemical fractions of DOM associated with high THM and/or HAA formation are associated with DOM source by measuring the proportion of these fractions in DOM collected from catchments with contrasting landcover types over three seasons.

III. Test our predictions drawn from objectives 1 and 2 by measuring the THM and HAA formation potential of NL drinking water supplies which are predicted to have either low or elevated formation potentials for these two classes of DBP based on watershed landcover.

Each of these goals represents a key step in evaluating one critical set of factors that likely regulate DBP levels in the drinking water in NL and importantly whether this regulation differs for two important class of DBPs (i.e. THMs and HAAs). Further, our understanding of the role of DOM source and its composition in regulating the formation of DBPs will aid us further in determining the chemical composition of precursors for HAA and THM formation. Understanding the general chemical or functional composition of DBP precursors will provide us with critical information needed to make decisions on the most efficient, safe and economical techniques for drinking water treatment particularly in rural NL communities. Further, if a link between DOM chemical fractions with high DBP formation potentials and DOM source is established it will provide a broader tool for DBP management that would not require detail DOM chemical fractionation for each water supply but rather reliance on watershed compositional data that the province already has.

Summary and Deliverables:
In summary we have found good evidence to suggest that watershed source of DOM could be an important factor regulating the wide range of DBP levels in drinking water across the province. We have the baseline data and our continued research will incorporate an additional new graduate student (Ms. Jennifer Bonnell) who will conduct both more specific chemical compositional analysis of the DOM used in Ms. Hannan's controlled experiments. Ms. Bonnell was recruited from the Water Resources Division in the NL government and has expressed keen interest in linking her dissertation research, which is focused on assessing the chemical composition of surface water DOM in NL, with the goals of this long term program to assess the factors regulating the levels of DBPs in NL drinking water. Both students will also incorporate investigations of key water supply sources chosen from the analysis of data completed from this study. Given our results and consultations with the Water Resources Division staff we will now incorporate the use of specific chemical fractions into these experiments to more directly assess components that may be have the highest formation potentials. This will future research will provide information to direct choices in the types of drinking water treatment used in smaller, rural communities to reduce the risks associated with DBP contaminants. Given our current work on DOM chemical composition and Susan's completion of samples ready for GC-ECD analysis we should be well poised to answer these new questions that are more directed at the needs of the province's drinking water quality program.

Specific deliverables provided to date:

Presentions at local and regional meetings/workshops:

Hannan, S., Huelin, S. and S.E. Ziegler Investigating the factors controlling chlorine disinfection byproduct (CDBP) formation in drinking water supplies of boreal watersheds" Atlantic Provinces Council on Sciences (Environmental Sciences), March 14-15, 2009, University of New Brunswick, Fredricton, NB.

Hannan, S., Huelin, S. and S.E. Ziegler (2008) Investigating the factors controlling chlorine disinfection byproduct (CDBP) formation in drinking water supplies of boreal watersheds. Second Annual Memorial University Dialog on Advancing Global Sustainability, St. John's, NL, Nov 24-25, 2008.

Huelin, S. and S.E. Ziegler (2008) Examining the role of dissolved organic matter source in the formation of chlorine disinfection byproducts (CDBPs). American Society of Limnology and Oceanography Summer Meeting. June 8-13, St. John's, NL, Canada.

Proposals submitted and/or funded to extend this research:

"Assessing the role of dissolved organic matter source and composition in regulating the yield of disinfection byproduct contaminants in NL drinking water supplies." S. Ziegler, Institute for Biodiversity and Ecosystem Science and Sustainability, Department of Environment and Conservation. Submitted with letter of support from Water Resources Division of the NL. Submitted October 30, 2009.

"A study of watershed-to-estuary nutrient and contaminant transport toward a monitoring system for assessing human impact in the Humber River Basin." S. Ziegler with E. Merschrod, C. Bottaro, and K. Hawboldt, Humber River Basin Project. Funded for April 2009-2011.

Additionally, this project has drawn the interest of an employee of the Provincial Department of the Environment who is now enrolled in the new Environmental Science PhD programme at MUN and will begin her programme January 5, 2009.

Future Deliverables following completion of analyses once GC-ECD is operational and/or funds are found to have samples analyzed by an outside laboratory:

MSc Thesis and publication by Susan Hannan

Components of PhD dissertation and publications by Jennifer Bonnell

We anticipate providing results of our findings in the Municipal News which goes out to about 2,000 municipal leaders and another 1,000 people in provincial and federal government and private sector. Jennifer Bonnell will be applying her water quality and GIS expertise and will receive training in biogeochemistry to address this broader project aimed at understanding DOM chemistry and its role in the generation of drinking water contaminants. Our hope is to expand upon this current research programme to more thoroughly address questions relevant to the management of water resources and drinking water quality in the province.


N

THE LESLIE HARRIS CENTRE OF REGIONAL POLICY AND DEVELOPMENT
1st Floor Spencer Hall, St. John's, NL Canada A1C 5S7
Tel: 709 737 6170 Fax: 709 737 3734 www.mun.ca/harriscentre

THE HARRIS CENTRE
Memorial University

THE HARRIS CENTRE
Memorial University