DOWN-THE-DRAIN GEOSPATIAL FATE MODEL FOR SUBSTANCES IN CONSUMER PRODUCTS

A pilot study for the provinces of Quebec and Ontario

Final Report

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Executive summary

In 2006, the Government of Canada announced the Chemicals Management Plan (CMP) for addressing the legacy of unassessed chemical substances in Canada. As part of the CMP, the Government of Canada has committed to addressing approximately 4300 substances prioritized through the Categorization process by 2020. Substances persistent in the environment and/or bio-accumulative substances toxic to humans or other organism need a screening mechanism to identify potentially harmful concentrations in surface waters. However, currently there is no pan-Canadian tool available to predict aquatic concentrations of substances released from wastewater systems across the country that is geospatially explicit (i.e. based on a river network to account for upstream contributions from other wastewater systems) at sufficient spatial resolution, and that is based on publicly available data to support risk assessment activities.

Between October 2012 and March 2013, a pilot study was carried out on behalf of Health Canada to test the feasibility of developing a large-scale contaminant fate model for the provinces of Quebec and Ontario. Using the best currently available hydrographic and geospatial information within a Geographic Information System, a new hydrological and chemical routing model was set up and tested for the study area. After incorporating the geo-location of more than 1000 wastewater treatment plants (WWTPs) and expanding the model to include lake processes within the river network, the cumulative effect of municipal wastewater effluents on surface waters was assessed, and a set of indicators of water contamination was created. These indicators included the predicted environmental concentrations (PECs) of contaminants in rivers and streams; the relation between the discharge of WWTPs and river flow as an indicator of dilution; and the percentage of wastewater in the river course. An analysis of the sensitivity and uncertainty of the model, as well as a validation of the model results against measured river flows and reported concentrations from literature revealed an acceptable model performance and errors within expected margins which are deemed suitable for the envisioned applications. Shortcomings exist for several process simulations (e.g., lake routing; human flow alteration) and, most importantly, are related to the availability and reliability of input data and associated parameter settings (e.g., location of contamination sources; substance removal rates; decay functions).

Given the overall positive validation results, we have high confidence that the model, if completed and spatially expanded, will be capable of predicting chemical concentrations in the Canadian river network for a variety of substances at a scale and quality suitable for screening and risk assessments. The model results provide quantitative and qualitative indicators at the river reach scale at 500 meter spatial resolution, which makes it suitable for both local-scale decision making and large-scale comparisons. The derived indicators can help to identify rivers and locations of high risk of exposure, and can contribute to the development of methodologies and tools for exposure assessments under the CMP. Furthermore, there is a potential to facilitate the prioritization of actions, such as reducing the sources of contamination, upgrading WWTPs, or protecting drinking water plants. In the long-term, there is also a large potential to conduct novel research at the Canadian scale, including the fate of emerging contaminants, such as nanomaterials, the effects of climate change and population growth on river contamination, or modeling under pandemic scenarios.

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1.   Introduction

On December 8, 2006 the Government of Canada announced the Chemicals Management Plan (CMP) for addressing the legacy of unassessed chemical substances in Canada with the goal of significantly reducing their potential risks to human health and the environment. As part of the CMP, the Government of Canada has committed to addressing approximately 4300 substances prioritized through the Categorization process by 2020. To date, some of these substances have been or are being addressed through the Challenge to Industry, the Petroleum Sector Stream Approach, and other initiatives.

Of the list of priorities from the Categorization process, a number of substances still remain to be addressed. In October 2011, Health Canada (HC) and Environment Canada (EC) announced a proposed class assessment approach with plans to assess and manage, where appropriate, the potential health and ecological risks associated with nine groups of substances. This initiative began with a Notice of Intent for the aromatic azo- and benzidine-based substance group, published on June 5, 2010. On October 8, 2011 an announcement that applies to this group and eight additional groups of substances was published in the Canada Gazette (Part I: Vol. 145, No. 41)[1]. The initiative includes:

- Aromatic azo- and benzidine-based substances
- Boron-containing substances
- Certain internationally classified substances with potential for exposure to individuals in Canada
- Certain organic flame retardants
- Cobalt-containing substances
- Methylenediphenyl Diisocyanates and Diamines (MDI/MDA)
- Phthalates
- Selenium-containing substances
- Substituted diphenylamines

More information is available on the Chemical Substances website[2].

Effluents from wastewater systems represent one of the largest sources of pollution, by volume, in Canadian waters. Negative impacts to aquatic ecosystems and to Canadians from harmful

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[1] **http://www.gazette.gc.ca/rp-pr/p1/2011/2011-10-08/html/notice-avis-eng.html**

[2] **http://www.chemicalsubstanceschimiques.gc.ca/group/index-eng.php**

substances found in wastewater effluents have been documented domestically and internationally for over 20 years[3]. Persistent and/or bio-accumulative substances toxic to humans or other organisms need a screening mechanism to identify potentially harmful concentrations in surface waters.

Currently there is no pan-Canadian tool available to predict aquatic concentrations of substances released from wastewater systems across the country that is geospatially explicit (i.e., based on a river network to account for upstream contributions from other wastewater systems) at sufficient spatial resolution and that is based on publicly available data to support risk assessment activities. Hence, there is a desire to develop an exposure model to support risk assessments of substances in down-the-drain products released by wastewater systems in Canadian waters. In this pilot study, we investigate the feasibility and requirements of developing an appropriate methodological framework for such a model.

As a first tier of model development, we build upon an existing large-scale geospatial risk exposure model for down-the-drain contaminants that was developed at McGill University for the lower St. Lawrence River Basin and expand the geographic scope to the entire provinces of Quebec and Ontario. The methodological approach involves applying a downscaling method to create seamless stream discharge values for the entire study region at high spatial resolution, i.e. 500 meter (500m); to employ a hydrological routing model to enable transport of chemical substances down the river network; to conduct a preliminary evaluation of the discharge and routing model; and to use existing field measurements (as available) to evaluate the mass balance model for both provinces. The results are aimed at supporting the development of exposure tools for chemical risk assessments under the CMP. The specific goals are to:

- Evaluate the existing hydrological routing model to generate distributions of dilution factors and river discharge that could be used to represent dilutive capacity;
- Evaluate the existing chemical mass balance model to generate distributions of contaminant concentrations for risk assessment purposes;
- Expand the current exposure tools to create a geospatial model covering all of Quebec and Ontario.

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[3] **http://www.gazette.gc.ca/rp-pr/p1/2010/2010-03-20/html/reg1-eng.html**

2. Study area

The study area is comprised of the Canadian provinces of Quebec and Ontario (Figure 1). For the hydrological discharge calculations, we also include all river reaches ('contributing areas') that enter the two provinces, as defined by the watershed delineation from the HydroSHEDS database (see Methods) in order to generate a hydrologically complete river network. Cross-boundary watersheds include parts of the United States from Minnesota, Wisconsin, Michigan, Ohio, New York, and Vermont, but most of these US watersheds drain into the Great Lakes before their flow arrives in Canada. In the current pilot study we assume complete dilution of contaminants in large water bodies, hence the US tributaries to the Great Lakes are considered not to pose an immediate risk for Ontario and Quebec. In terms of chemical mass balance calculations, we thus exclude effluents from wastewater treatment plants located in contributing areas south of the Great Lakes. There are, however, parts of New York and Vermont that drain directly into the lower St. Lawrence River and that are likely more relevant sources of contaminants from the US, so we included these regions in the pilot model version.

Figure 1: Study area: Quebec, Ontario and hydrologically connected areas

3.   Methods

3.1 Discharge model and validation

In order to simulate environmental contaminant concentrations, an adequate characterization of discharge of Canadian rivers that receive wastewater effluents is necessary. This ensures that the dilutive capacity of receiving waters is appropriately parameterized to generate predicted environmental concentrations that are suitable for contaminant risk assessments.

The baseline hydrographic data for the discharge routing model used in this project is provided by the HydroSHEDS database (Lehner et al. 2008), a publicly available global suite of data layers representing river network topology and watershed boundaries. HydroSHEDS defines flow directions at 500m pixel resolution which are used for transport simulation of water and substances in a routing model called HydroROUT that is currently under development at McGill University (Lehner and Grill 2013). To be able to represent lakes, HydroROUT links the river lines of HydroSHEDS with the vectorized lake polygons of the Surface Water Body Database (SWBD; NASA-NGA 2003) which were digitized as part of the Shuttle Radar Topographic Mission (SRTM) at 30m resolution. It should be noted that HydroSHEDS and SWBD provide high-quality information only up to 60º northern latitude; beyond that, the underlying digital elevation model is currently substituted with lower quality data (i.e., HYDRO1k by USGS).

In the current version of HydroROUT, discharge is derived by accumulating land surface runoff along the river network, yet the underlying simulation of runoff generation (i.e., the vertical water balance) is not performed within the model itself. Instead, we employ decoupled, external runoff estimates provided by the global integrated water balance model WaterGAP (Alcamo et al. 2003, Döll et al. 2003; model version 2.1 as of 2012[4]).

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[4] Note that the WaterGAP model has since undergone several updates, yet the most recent version 2.3 was not available in time for being integrated in this pilot study.

WaterGAP provides runoff estimates of long-term monthly averages for the period of 1961-90 (i.e., the 'climate-normal' period as defined by the World Meteorological Organization) at 0.5 degree grid resolution. We spatially downscaled these runoff estimates by disaggregating the large grid cells into 500m pixels and then accumulating them along the HydroSHEDS river network. In order to evaluate the accuracy and uncertainty associated with the HydroROUT model, we compared our downscaled discharge estimates with the reported values of HYDAT gauging stations (Environment Canada, 9th release, November 2012; for further details see section 3.1.2 below).

3.1.1 Data preparation

By means of the Environment Canada Data Explorer, average daily stream flows of gauges in the provinces of Quebec and Ontario were extracted from the Water Survey of Canada dataset[5] in a time series format. Location information is provided for all gauging stations as coordinates in decimal degrees. The HYDAT gauging stations had to be co-registered (i.e., snapped) to the stream network of HydroROUT to allow for the assignment of simulated long-term average monthly flows and upland area from the model to each station. With the use of provincial dam and reservoir data, gauging stations in close proximity to potential sources of flow regulation were flagged accordingly; yet it is important to note that this information was not readily available for Ontario, thus only Quebec rivers were attributed for the presence of dam structures in near vicinity. Finally, the difference in upland watershed area between the reported values of the HYDAT stations and the simulated values based on HydroSHEDS was calculated. This difference serves as a measure of accuracy for the co-registration of the HYDAT gauging station to the HydroROUT stream network.

For the subsequent validation purposes, different subsets of stations in the provinces of Quebec and Ontario were selected by extracting them from the total of 522 available stations. In particular, a set of 57 "most reliable" stations was derived based on the following, consecutive criteria:

1. Stations need to have 30 years of observed, uninterrupted records in the study period (1961-90) – *number of stations reduced to 235*

2. Stations need to show a difference of maximum 10% between reported HYDAT and estimated HydroSHEDS watershed area – *number of stations reduced to 156*

3. Stations cannot have a known major dam or reservoir in close proximity – *number of stations reduced to 57*

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[5] **http://ec.gc.ca/rhc-wsc/default.asp?lang=En&n=9018B5EC-1**

Additional validation sets with more HYDAT stations and different criteria have also been evaluated (see Tables A-1 and A2, as well as Figures A-5 and A-6 in the Appendix for results).

The R statistical software and its HydroTSM package[6] were used to calculate statistics relevant to the validation of the modeled discharge data. Daily and monthly statistics were calculated for each HYDAT station from daily flow data during the study period. For the HydroROUT model, only monthly statistics were calculated from the long-term average monthly flow data. The following hydrological indicators were assessed for observed flows (HYDAT) and simulated flows (HydroROUT):

- MQ: long-term average flow for time series 1961-90

- Annual flow regime: series of 12 representative monthly flow values (Jan-Dec) representing the average flow for each month calculated from the period 1961-90

- Q90: daily flow that is exceeded at 90% of time (only calculated for HYDAT data)

- Q90-Month: average flow of the lowest month in the annual flow regime (see above)

3.1.2 Discharge comparisons

To evaluate the general quality of HydroROUT's discharge estimates, long-term average flows were compared across stations using a linear regression analysis. In a second comparison, the ability of the HydroROUT model to simulate the annual flow regime was tested using the Nash-Sutcliffe Efficiency (NSE) as the quality indicator.

The risk from chemical substances in surface waters is usually assessed under low flow conditions for which Q90 is a frequently used indicator. Typically, Q90 is calculated from daily discharge measurements, but as the WaterGAP runoff estimates are given as monthly time series, we approximated (daily) Q90 with a substitute, namely Q90-Month (for the definition see section 3.1.1 above). To explore the validity of this approach, we first assessed the relationship between Q90 and Q90-Month for observed HYDAT flows by performing a linear regression analysis, and then applied a second linear regression to test the correlation of Q90-Month between observed HYDAT and simulated HydroROUT values.

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[6] **http://cran.r-project.org/web/packages/hydroTSM/hydroTSM.pdf**

3.2 Wastewater treatment plants

3.2.1 Data sources and pre-processing

Data and metadata about municipal wastewater treatment plants (WWTPs) have been collected from various sources. All data gathered for the current version of the model was either obtained by making public requests or by extracting data from surveys publically available online. The geospatial locations and relevant attributes for wastewater treatment plants located in Quebec and Ontario were obtained from provincial ministries. The dataset of treatment plants for Quebec and Ontario is assumed to be comprehensive for human/household waste, i.e. all available WWTPs have been included. Non-confidentiality has been confirmed. For wastewater treatment plants located in Vermont and New York, geospatial locations and relevant attribute data were extracted from the USEPA's Clean Watersheds Needs Survey (USEPA 1996; updated data for 2010).

Due to the different data providers, the received tables did not share a common structure and differed in storage units and information content (including their metadata). To homogenize the data, we created a Microsoft Access database which keeps the original information from each province in separate tables and developed a query which allows for the generation of one common table as an input source to the fate model.

3.2.2 Georeferencing of WWTPs

All WWTPs located in the study area were co-registered in reference to the HydroROUT river reach network. The purpose of this re-allocation effort was to adjust for possible errors in either the coordinates of the WWTPs, in the HydroSHEDS network representation, or in both. In this preprocessing step, each treatment plant was assigned to the river reach that best represents its topological location in the hydrological network.

In order to inform the re-allocation process, a satellite imagery base layer (Bing Maps) was used to visualize WWTPs, and a detailed vector layer showing labeled stream, river and lake networks (CanWater) was used for spatial reference. WWTP attribute data provided the name of the water body/feature receiving the WWTP discharge and thus enabled a guided allocation of the WWTPs to the most fitting river reach as represented by HydroSHEDS. If necessary, supplementary maps and reports from online sources were consulted for clarity. In the states of New York and Vermont, the USGS National Hydrography data set was used to identify and label stream and river networks. A comment field was populated in the case of remaining doubts following the consultation of all available information.

All WWTPs discharging directly into lakes or into a river reach within 2 km of a lake were given a specific code indicating this characteristic. Using the SWBD lake layer for reference, the lake IDs of the water bodies into which they discharge were recorded. In terms of available river flow for the dilution of effluents we then assigned the total flow at the outlet of the lake – representing the sum of all inflowing lake tributaries – to each respective lake WWTP. In the same sense, all WWTPs discharging into the estuary of the St. Lawrence River (which is not included in the landmask of HydroSHEDS) were also flagged with a unique code. The available river flow for these WWTPs was taken from the most downstream HydroSHEDS river reach draining into the estuary in order to represent the highest available modeled discharge; despite this approximation, the average dilution in the estuary of the St. Lawrence River is assumed to be underestimated.

3.2.3 Distribution of WWTPs and data limitations

Data was available for a total of 1283 WWTPs within the study area (Figure 2). Quebec has the most treatment plants with a total of 692, followed by Ontario with 473. The states of Vermont and New York in the contributing basin areas have 45 and 73 WWTPs, respectively. According to the records, the 1283 WWTPs discharge a total effluent volume of 13.8 million m^3 per day and serve a total population of 15.3 million people (see Table 2).
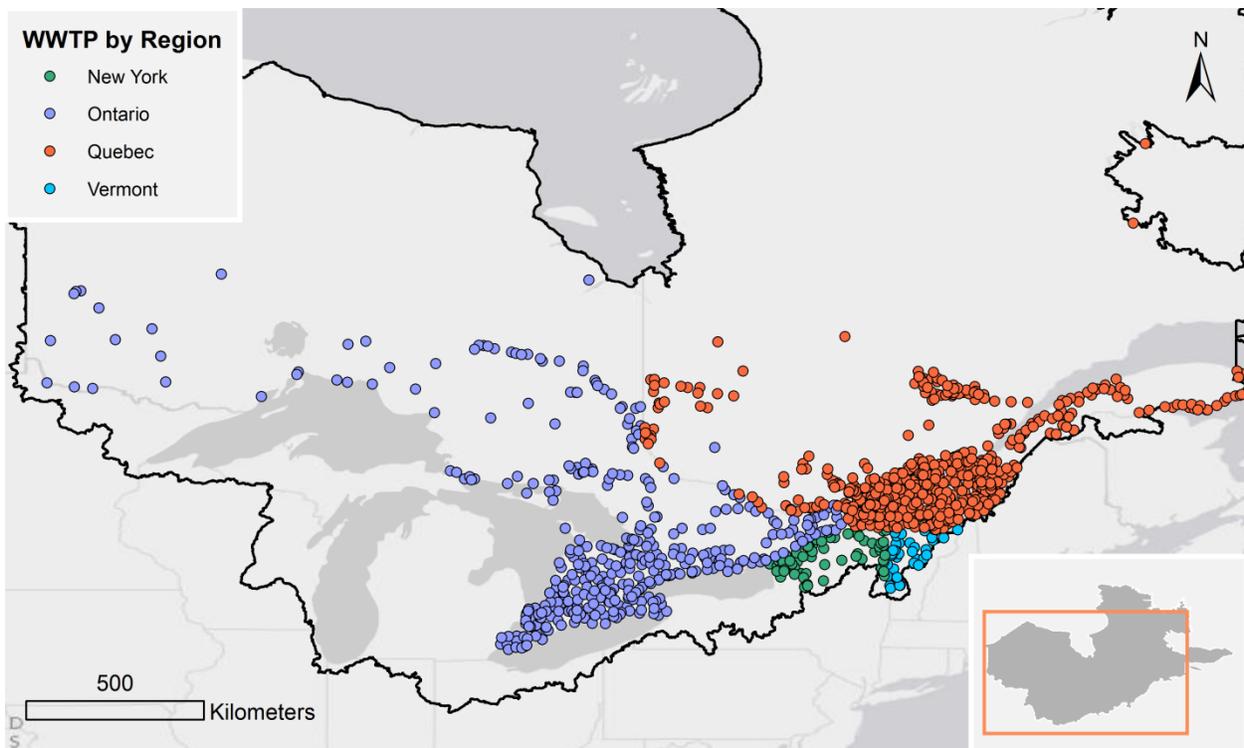
Figure 2: Distribution of wastewater treatment plants in the study area

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From the total of 1283 given treatment plants, we included 1196 in the current model and excluded 87 due to the following issues and limitations (note that multiple issues may occur for the same plant):

- The records of 16 treatment plants in Ontario indicated that they did not discharge directly into surface waters (or the treatment type was unknown); those plants were not included in the model.
- A total of 59 treatment plants that did not report numbers on the population served or on discharge were excluded from the study. A total of 46 WWTPs did not report the population served, 31 WWTPs did not report the plant discharge, and 18 WWTPs had unreported numbers for both discharge and population served. We expect little impact from this exclusion, since the plants excluded each serve no more than 1,000 people (an average of 181 people) and discharge no more than 5400 m³/day (an average of 881 m³/day).
- Coordinates were missing for 72 stations in Ontario and we approximated the location of 29 of these treatment plants using their given addresses.
- A total of 18 treatment plants reported only periodical discharge, which implies that the effluent load should not be expected to occur year-round. The dilution factors from these treatment plants may be too high for parts of the year, resulting in an underestimation of the concentrations in the river. We marked these treatment plants for the calculation of the dilution factors. We did, however, include the load from these treatment plants in the current model.

3.2.4 Wastewater treatment types

We conducted a review of the relevant attributes of WWTPs compiled for Quebec, Ontario, New York and Vermont in which we re-assessed the treatment classification coding of WWTPs in consultation with Health Canada and Environment Canada into the five categories outlined in Table 1.

Table 1: Assigned treatment types

Previous treatment types	Adjusted treatment type (this project)	Coding
No treatment	No treatment	0
Primary treatment	Primary treatment	1
n.a.	Lagoon treatment	1a
Secondary treatment	Activated sludge	2
n.a.	Trickling filter	2a
Tertiary treatment	Tertiary treatment	3

Table 2: Summary statistics of discharge volume, population served, and number of WWTPs by province/state

Treatment Type	Ontario	Quebec	New York	Vermont	Grand Total
No treatment					
Discharge (m³/day)	4,195	39,238			43,433
Population served	1,708	44,002			45,710
Number of stations	5	63			68
Primary treatment					
Discharge (m³/day)	535,395	3,628,418	14,896	42	4,178,750
Population served	533,873	2,734,625	24,805	366	3,293,669
Number of stations	21	35	25	1	82
Lagoon treatment					
Discharge (m³/day)	224,181	1,473,220	9,539	8,487	1,715,427
Population served	299,551	1,915,737	10,213	18,171	2,243,672
Number of stations	171	516	9	12	708
Activated sludge					
Discharge (m³/day)	6,019,814	626,299	29,583	4,471	6,680,167
Population served	7,414,725	735,791	34,759	9,077	8,194,352
Number of stations	232	37	23	2	294
Trickling filter					
Discharge (m³/day)	103,983	651,841	41,185	9,615	806,624
Population served	115,852	885,881	35,121	7,831	1,044,685
Number of stations	11	30	6	1	48
Tertiary treatment					
Discharge (m³/day)	39,582	101,210	66,699	97,016	304,507
Population served	41,012	138,846	67,435	183,279	430,572
Number of stations	17	11	10	29	67
Non-surface discharge or treatment type unknown					
Discharge (m³/day)	82,612				82,612
Population served	57,570				57,570
Number of stations	16				16
Total discharge (m³/day)	**7,009,762**	**6,520,226**	**161,902**	**119,630**	**13,811,520**
Total population served	**8,464,291**	**6,454,882**	**172,333**	**218,724**	**15,310,230**
Total number of stations	**473**	**692**	**73**	**45**	**1,283**

3.2.5 WWTPs discharging into lakes

According to the available data, 221 WWTPs discharge a total volume of 4.5 million m^3 per day into 89 lakes across the four provinces/states. Table 3 shows the breakdown of WWTPs that discharge into lakes by region, and Table 4 lists statistics for all lakes with WWTPs. The Great Lakes alone (Lake Ontario, Lake Michigan-Huron, Lake Erie and Lake Superior) account for 94 WWTPs.

Table 3: Volume of wastewater directly discharged into lakes by region

Region	Number of WWTPs discharging into lakes	Volume wastewater discharged (m³/day)	Population served
Quebec	44	71,153	108,717
Ontario	149	4,405,978	5,468,433
Vermont	7	25,764	55,903
New York	21	45,512	45,512
TOTAL	221	4,548,407	5,679,571

Table 4: Statistics of lakes that receive direct discharge from WWTPs

Lake Name	Nr. of WWTPs discharging into lake	Total population served	Volume of WWTP discharge received (m³/day)	Lake surface area (sq. km)
Lake Ontario	46	4,576,034	3,509,777	19,347
Lake Michigan-Huron	31	190,515	180,729	117,120
Lake Champlain	12	75,793	50,605	1,141
Lake Erie	12	57,685	88,072	25,767
Lake Simcoe	7	107,065	100,901	759
Lac St. Jean	5	15,455	11,896	1,066
Lake Superior	5	110,388	116,869	81,843
Lake Timiskaming	4	7,055	6,520	204
Lac Aylmer	3	5,480	4,213	32
Lake Muskoka	3	6,408	4,135	115
Buckhorn Lake	2	2,452	3,373	109
Lac Magog	2	3,655	1,195	11
Lac Megantic	2	440	110	27
Sturgeon Lake	2	16,993	18,547	43
Other Lakes (total 78)	85	504,153	451,464	4,904
TOTAL	221	5,679,571	4,548,407	252,488

3.2.6 Calculation of dilution factors

Dilution factors for each WWTP are calculated as the ratio between the modeled river flow of HydroROUT at the location of the WWTP and the reported discharge leaving each WWTP.

$$DF = \frac{v_{River} + v_{WWTP}}{v_{WWTP}}$$

where v_{River} is the average flow volume in the river reach where the treatment plant is located, and v_{WWTP} is the effluent volume from the sewage treatment plant.

The resulting distribution of the dilution factors as a cumulative probability curve is shown in Figure 17 (section 4.3) while Figure 18 displays the dilution factors under low flow conditions.

3.2.7 Calculation of percent wastewater in river

The wastewater flow expressed as a percentage of river flow is an indicator that provides general information on the status of a river with regard to cumulative WWTP effluents and can help identifying critical locations with a high proportion of effluents in the river water. The percentage of wastewater in the watercourse is estimated on the basis of reported average river flow and the accumulated effluent volume from all upstream WWTPs:

$$PercentWastewater = 100 \cdot \left(\frac{v_{WWTP}}{v_{WWTP} + v_{River}} \right)$$

where v_{River} is the average flow volume in a river reach, and v_{WWTP} is the accumulated effluent volume from all wastewater treatment plants upstream of the river reach.

We accumulated the effluent flow from WWTPs along the stream network and applied the above formula for each river reach. We set the total effluent discharge to zero if a major lake (as defined by the lake routing threshold) was reached. The same procedure was followed for the chemical mass that reached a lake, i.e. the mass was set to zero (see 3.4.8 below).

We calculated the percent wastewater indicator only for low flow conditions (see results in Figure 19).

3.3 Drinking water plant integration

The Drinking Water Surveillance Program (DWSP) operated by Ontario's Ministry of Environment monitors the quality of drinking water in the province of Ontario. The program collects water samples from raw water, treated water, and water distribution systems which are then subjected to tests for chemical, physical and radiological parameters. The DWSP provides key information on drinking water sources in Ontario including: the approximate location of drinking water sources; the name of drinking water treatment plants; and the water bodies (lake or river) from which they source water. Based on this information, DWSP sampling points were co-registered to the HydroSHEDS river network (in a similar process as described for WWTPs) with the intention of identifying drinking water intake points (DWIPs) representing the location and type of drinking water sources in Ontario. Once allocated, the DWIPs can be combined with the fate model to allow for a first-level identification of DWIPs at high risk of contaminant exposure.

DWIPs were generated from a shapefile of point locations of drinking water treatment plants available for download from Environment Canada's DWSP dataset. For our pilot study, we assumed close proximity between a drinking water treatment plant and its actual water intake. A total of 122 DWIPs were co-registered of which 50 were located either at the shore or within 2 kilometers of 18 different lakes. For cases in which water is sourced from lakes, the lake ID of the lake from which water is withdrawn was recorded. In these cases the level of contaminants is represented by the river reach at the lake outflow, which we assumed to be zero for large lakes.
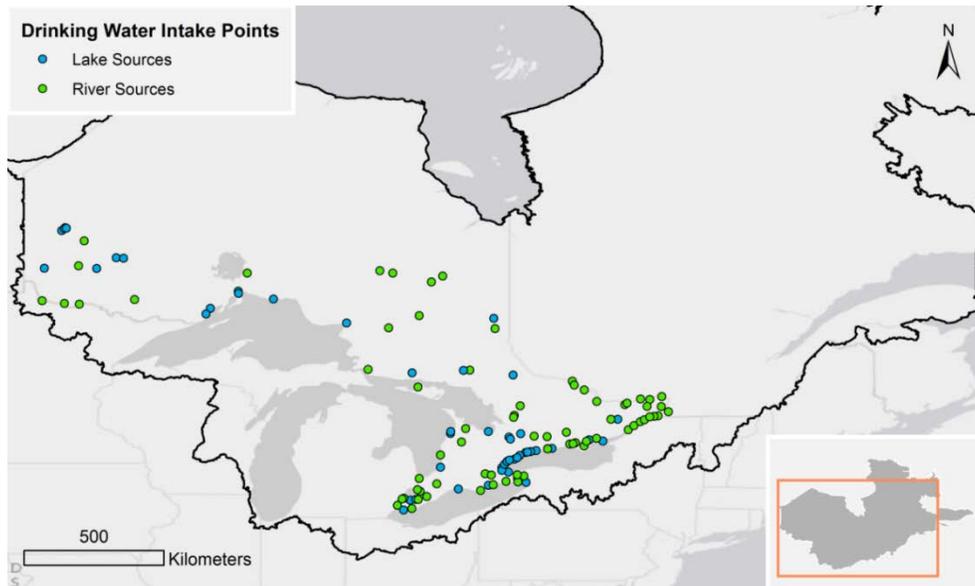
Figure 3: Drinking water intake points in the province of Ontario. It is assumed that the location of drinking water treatment plants reported in the DWSP dataset is geographically close to the actual drinking water intakes.

3.4 HydroROUT and contaminant fate model

For this study, a previously developed hydrological river routing model called HydroROUT (for a basic description see Lehner and Grill 2013) was used which provides GIS-based hydrography, attribute data, and routing capabilities. It is combined with a contaminant fate module which was specifically adjusted for the study area of Quebec and Ontario.

HydroROUT is integrated with the commercial GIS software package ArcGIS. The first function of HydroROUT is to establish hydrologic connectivity, which is achieved by following the concepts of 'schematic links' and 'geometric networks', i.e. a directed network graph located in an ArcGIS Geodatabase. Geometric networks are normally used to model infrastructure, such as electric utility lines and sewer systems, but they are also well suited to represent connectivity within dendritic river networks. Geometric networks are collections of line objects (e.g., river reaches) and point objects (e.g., locations of confluences of two river reaches) that possess a connectivity relationship based on the coincidence of the start- and endpoints of the river reaches. The connectivity information between river reaches and other objects are stored in connectivity tables, the so-called logical network. River reach geometries can thus be treated as individual elements for use in tracing and flow operations.

The second function of HydroROUT's processing engine is the routing of substances downstream the river network, which may include the accumulation of mass from different distributed sources in the river network (e.g., WWTPs) and/or constant or time-dependent decay functions that diminish the substance to be accumulated gradually along its path.

River reaches are the finest scale on which HydroROUT operates. At the 500m resolution, there are more than 400,000 river reaches with an average length of 2.8 km within the study area. Figure 4 shows the simplified river network representation of HydroROUT for the study area; note that small streams are removed for clarity of presentation. Basins were delineated for the study area to facilitate summarizing the results per basin. First order basins are marked with shades of blue. A total of 158 major rivers have been labeled with names using the Times Atlas[tm] as part of the HydroSHEDS project and additional local rivers have been mapped for this project.

During the routing process, lakes and reservoirs are considered objects treated differently than river reaches, primarily due to their different nature representing mixing, flow velocity, depth and volume. Lakes are more appropriately modeled as 'completely stirred reactors' (Butkus et al. 1988). The concentration of constituents in a lake is determined by the inflow concentration, a decay factor, and the volume of the lake.
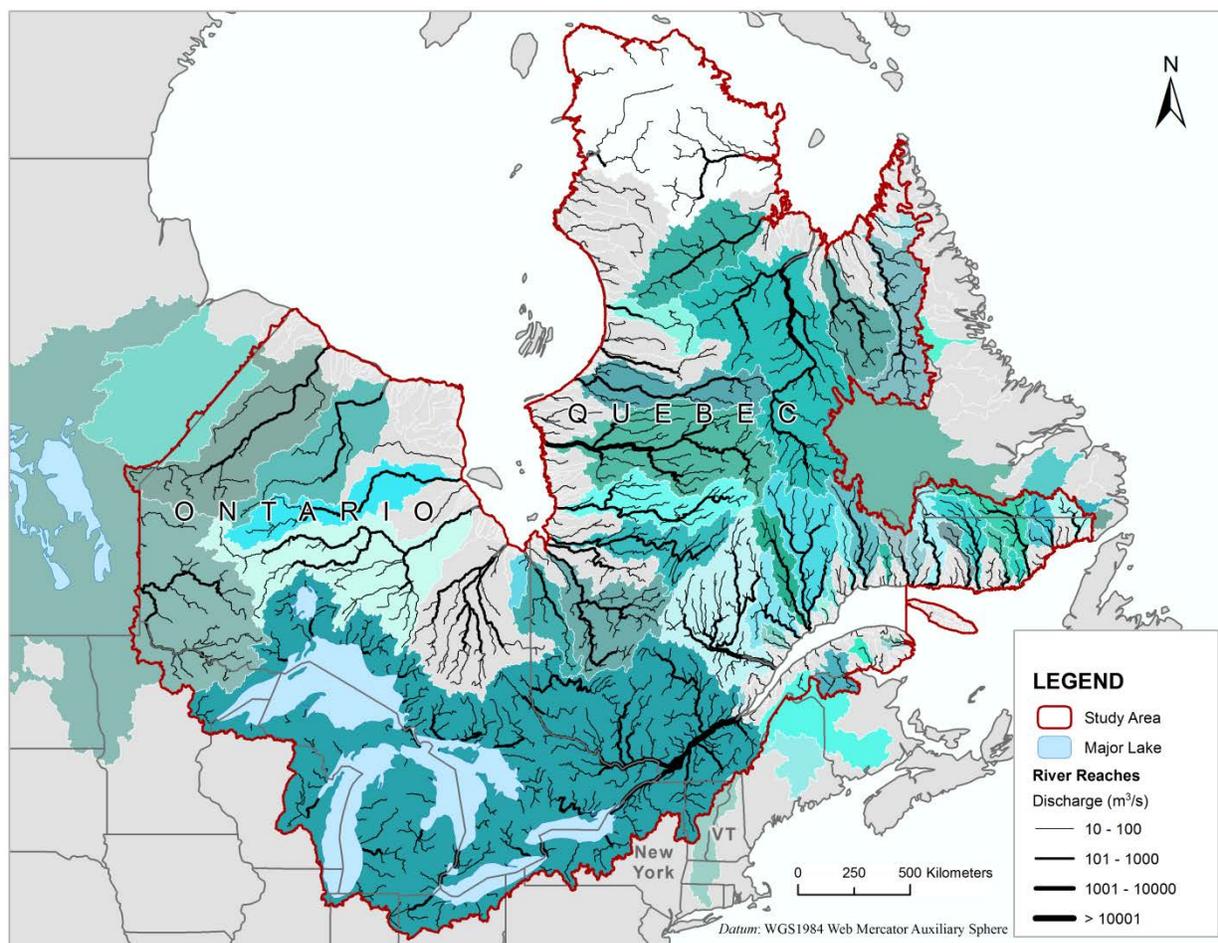
Figure 4: Major river basins (colored in shades of green and blue) and river network in the study area, derived from the HydroSHEDS database.

3.4.1 Conceptual model

Aquatic concentrations of substances released from wastewater systems can be adequately computed based on calculations of consumption, removal in treatment plants, and degradation in the environment (Pistocchi et al. 2010). A conceptual model of the fate model as applied in this project is shown in Figure 5.

3.4.2 Per capita substance consumption and metabolization

Reasonable estimates of mass input can usually be obtained from the product of average per capita consumption (generated from sales data) and estimated population, adjusted for human metabolic reduction, if relevant, and possible removal in sewage treatment (Keller et al. 2006). However, for numerous reasons, not all pharmaceuticals that are sold are actually consumed by the user. We could not find reliable quantitative data on the fraction of unused medication; so as a worst-case scenario it was assumed that the volume sold was the same as the volume consumed.

Figure 5: Conceptual model

Our mass balance model uses the number of people served per treatment plant as reported by the data providers. The multiplication of these population numbers by the assumed per capita consumption provides the net consumption. A part of the net consumption may then be metabolized in the human body. This fraction needs to be defined by analysing relevant clinical data for each substance. The resulting down-the-drain portion enters the sewage system and is assumed to reach the municipal wastewater treatment plant.

3.4.3 Removal of substances during the treatment process in WWTPs

A portion of the mass of a substance may be removed by the treatment process. This depends on the nature of the substance and on the specific process applied in each treatment plant. We classified the treatment plants by expert judgment and some general guidance from Environment Canada into five categories: No treatment; Primary treatment; Lagoon treatment; Secondary treatment; and Tertiary treatment. The actual removal rate for each category depends on the substance. The removal rate for each treatment type (in percent) is an input parameter of the contaminant fate model.

3.4.4 Environmental release and river routing

In pollution routing, the dominant dilution mechanism is advection, which can be effectively modeled using stream length, velocity, discharge and a decay function (Pistocchi et al. 2010). The 'plug-flow' model as applied here is assumed to be an adequate and frequently used approach in pollutant routing at the river reach level (Feijtel et al. 1998, Anderson et al. 2004, Pistocchi et al. 2009) and is used in both the GREAT-ER (Feijtel et al. 1998) and the ISTREEM model (http://www.aciscience.org). ISTREEM uses GIS-Rout as part of the engine (Wang et al. 2000).

In our contaminant fate model, a 'plug' of substance mass (i.e., the amount of contaminants released from the treatment plant) is accumulated downstream as the sum of the input from the current and all upstream reaches flowing into the current reach. As a result of this process, steady-state annual average loadings are calculated.

3.4.5 Basic concept of flow routing

The river network is processed in the hydrological order from source to sink (see Figure 6). The outflow mass balance for each river reach is calculated as:

$$Reach_{i,out} = (\sum wwtp_{k...n,in} + \sum reach_{j...n,in}) * k$$

where $Reach_{i,out}$ represents the total mass at the end of the river reach, $wwtp_{k...n,in}$ represents mass influx from all wastewater treatment plants located anywhere on the river reach, $reach_{j...n,in}$ is the inflow from upstream reaches, and k represents the total reduction in mass due to environmental degradation processes, if applicable. The calculated $Reach_{i,out}$ values become input values in the next iteration step. k is the environmental decay factor and is calculated based on first-order decay (see section 3.4.7).
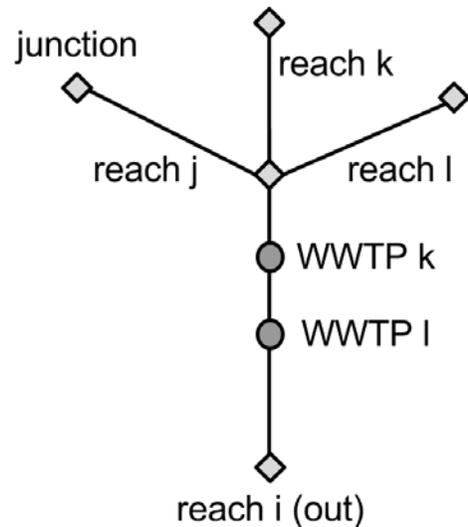
Figure 6: Simplified model of routing process

3.4.6 Flow velocity

Instead of using a constant velocity as in earlier model versions, for this study we implemented variable flow velocities. According to Allen et al. (1994) velocity can be estimated from bankfull discharge following the empirically derived formula:

$$v = 1.07 \cdot (Q^{0.1035})$$

where v is the velocity in m/s within the river reach and Q is the bankfull discharge in m^3/s.

Using HydroROUT's discharge estimates, this equation results in the highest flow velocities for the St. Lawrence River at roughly 2.8 m/s, the Riviere du Nord is approximated at 1.5 m/s, and the lowest velocities of very small rivers fall in the range of 0.7 m/s.

Previous version of the HydroROUT model operated with a fixed stream flow velocity of 1 m/s (as this value is also used by the underlying WaterGAP model to calculate global runoff estimates), which produced reasonable results at large scales. In the current version of HydroROUT, we implemented variable velocities expecting that this can improve the estimation of concentrations of substances with environmental decay (see next section), yet this is subject to further verification. Ideally, a physically based velocity estimate should be implemented.

3.4.7 Environmental decay

Many contaminants remain relatively persistent in the environment and are therefore considered conservative in terms of degradation, absorption and sedimentation. However, during the routing in the river network less conservative substances undergo transformation processes of degradation that may include decay, absorption and sedimentation to various extents. The degradation of a chemical substance in the river body is often expected to decrease at a rate proportional to its value, and can therefore be represented through an exponential decay model:

$$\frac{dN}{dt} = -kN$$

where N is the mass and k is a positive number called the decay constant. The solution to this equation is:

$$N(t) = N(0)\, e^{-kt}$$

where $N(0)$ is the initial mass at $t=0$ (i.e. when the pollutant enters a river reach), and $N(t)$ is the mass at time t (i.e. at the end of the river reach, when the pollutant has travelled through the entire river reach). In the river network, t is derived by dividing river reach length by the average

velocity within the river reach. This corresponds to the average retention time in each individual river reach, i.e. the time a plug of fluid needs to travel from the beginning to the end of the river segment.

After the model has processed every river reach in the model, the concentrations per river reach are calculated by dividing the accumulated chemical mass (*N*) by the discharge (*D*) of the reach plus the accumulated amount of water volume from the wastewater treatment plant (*V*) at time *t*:

$$C(t) = \frac{N(t)}{D(t) + V(t)}$$

3.4.8 Lake routing

Lakes are expected to dilute chemical concentrations and thus limit exposure risk depending on the lake's volume and residence time. Although lakes and large reservoirs are explicitly included in the HydroROUT model, it has not been part of this project to study their individual effects on the dilution, trapping, or delayed transport of substances along the drainage network. This is in part due to the lack of information on lake storage volumes. For large lakes (in particular the Great Lakes), the assumption is made that substances from WWTPs or rivers that directly discharge into them are not passed on downstream. For small lakes, the assumption is made that substances are passed on without delay, absorption, or decay. The user interface includes a field to enter a threshold size at which the mass balance becomes zero as a result of the lake's dilution effect.

Figure 7 shows the lake surface areas associated with each river reach. Note that each lake is assigned to one river reach only, specifically to the reach most downstream, which usually corresponds with the lake's outflow point.

Furthermore, Table 4 provides an overview of the lakes affected by effluent discharge. Depending on which threshold is set in the model, the load either gets completely eliminated, or is passed through the lake without elimination. If not stated otherwise, we used a rather arbitrary threshold of 100 km² for the model runs presented in this report, which should be verified by expert judgement and adjusted accordingly.
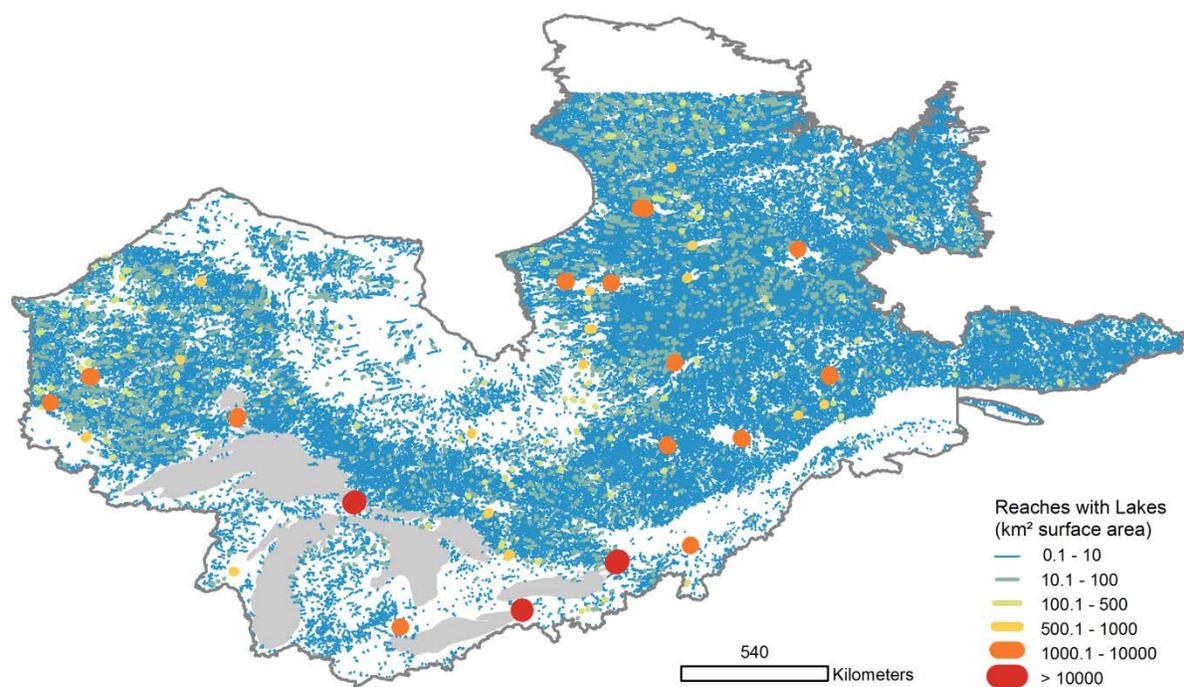
Figure 7: River reaches associated with lakes, and their respective lake sizes (note that the applied lake database has no coverage north of 60° degrees latitude)

3.4.9 Graphical user interface

The essential parameters discussed above can vary significantly across different substances, or need to be altered to explore the sensitivity and the response of the model. To facilitate this, we developed a simple graphical user interface that enables the user to create scenarios, i.e. simulation runs with specific settings (Figure 8).

Future plans for the HydroROUT model include implementation as a standalone executable file to further increase user friendliness and flexibility. This requires prior installation of an ArcGIS Standard edition on the computer where the model should run, as well as a set of pre-processed geospatial input data at a specific location in the file system.
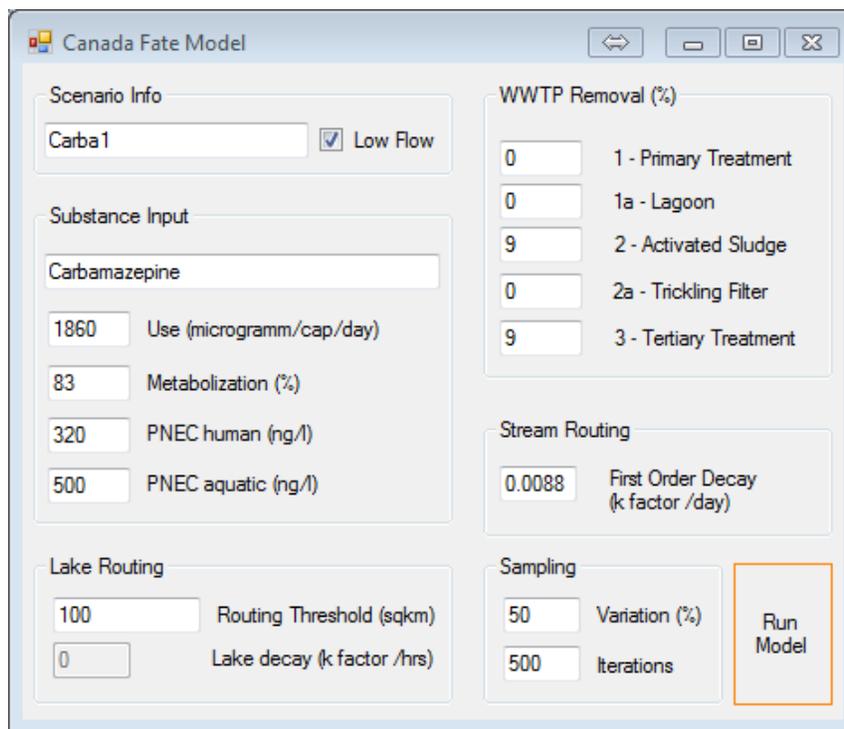
Figure 8: Graphical user interface; settings shown were used for the parameter sensitivity analysis

3.4.10 Model output

The contaminant fate model can be executed using the graphical user interface as shown in Figure 8. The model computes the number of simulations specified and saves the results in tables, which then can be linked to the existing river network and visualized using 'layer' styling files with predefined legends.

3.5 Mass balance validation and case study Carbamazepine

3.5.1 Limited data availability for mass balance validation

The performed evaluation of the mass balance model for Quebec and Ontario with geospatial monitoring data was dependent on the availability of suitable monitoring data for specific substances. To facilitate the evaluation process, Canadian surface water concentrations for a number of down-the-drain chemicals have been compiled through an extensive literature review (see Figure 9). However, the collected data, though useful to get a general idea about the performance of the model, does not allow for a systematic evaluation of our mass balance model.
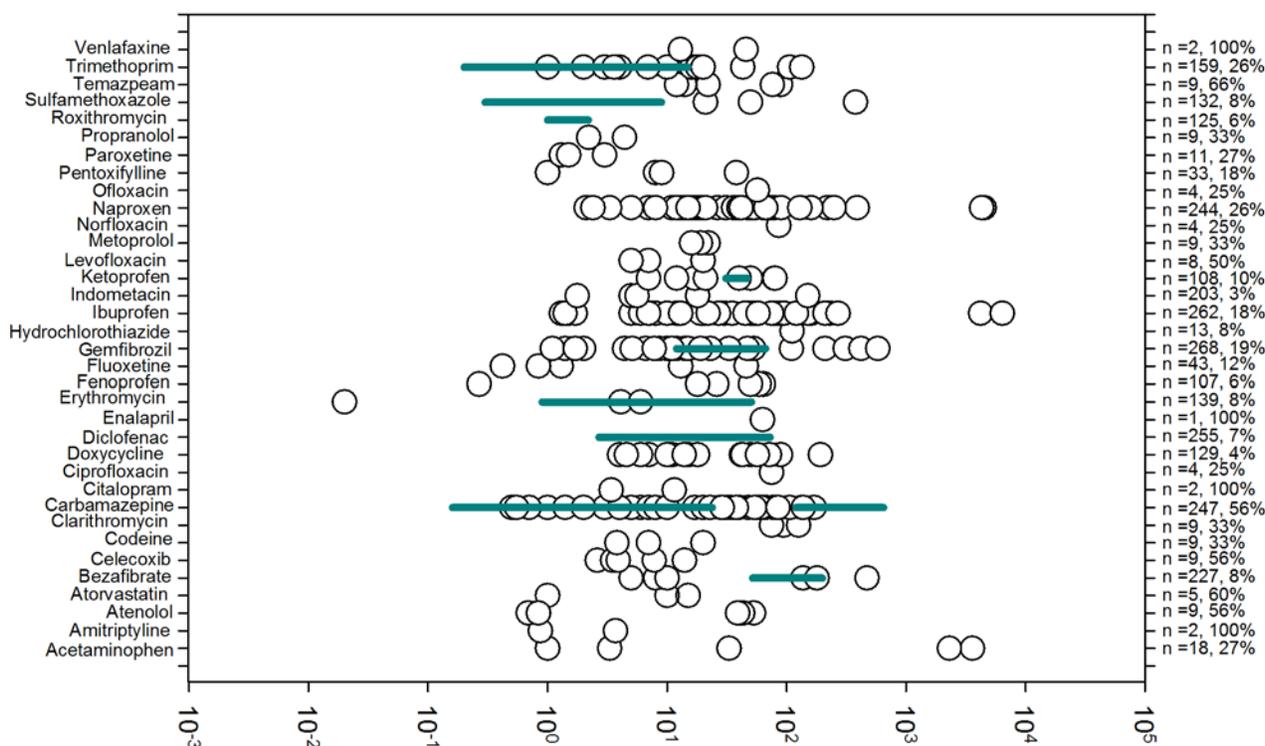
Figure 9: Meta-analysis of pharmaceuticals found in Canadian surface waters (Khan and Nicell, unpublished). The cirles represent individual samples, for which concentrations are given on the x-axis. The green lines represent studies that reported concentration ranges. *n* is the total number of samples that have been analyzed for the presence of a given pharmaceutical. The associated percentage refers to the frequency with which a given pharmaceutical has been detected. We extended this effort for Carbamazepine and now report 373 samples from Canadian surface waters with a 52% detection rate.

We were hoping that boron concentrations in surface waters could be used to validate our model, since there is a good amount of sample data available. Boron has been used for the evaluation of mass balance models, such as Greater-ER in Europe. However a study by the Canadian Council

of Ministers of the Environment (CCME 2009) reports that despite being used in other countries, such as the UK, where boron is sourced primarily from WWTP effluents, the source of boron in Canada primarily stems from the surrounding geology (WHO 2003; CCME 2009) making the chemical unsuitable for validating consumer-sourced substances.

Without suitable validation data, our model relies on the assumption that concentrations are adequately represented if the discharge model is suitable for the purpose of screening chemicals, and that the estimates of population input and environmental decay are correct. However, although some stable substances could possibly be represented well with our model, other substances that are subject to rapid degradation in the environment, or substances with non-uniform consumption among the population are difficult to validate without actual field measurements.

Despite the lack of a consistent sampling campaign, we applied several semi-quantitative methods to evaluate the performance of the mass balance module for the case study of **Carbamazepine**. Carbamazepine is a commonly prescribed drug in Canada, shows low removal in wastewater treatment plants and is characterized by persistence in surface waters (half-life ~70 days) making it a good candidate for the validation of our mass balance model. We used the substance Carbamazepine to test the sensitivity of our model with regard to process and parameter uncertainties, and we performed a simple mass balance validation. Carbamazepine is suitable because it is commonly detected in Canadian surface waters, and several studies exist in Quebec and Ontario, as well as throughout Canada.

The initial conditions to drive the mass balance model for Carbamazepine are shown in Table 5.

3.5.2 Sensitivity due to process uncertainty

We conducted an analysis to estimate the sensitivity of our model with regard to the different processes included in the model. First, we ran the model assuming no substance removal at all; we then sequentially introduced the different removal mechanisms (human metabolism, WWTP removal, lake removal, and in-stream decay) to estimate the effect on the shape and 95th percentile of the concentration distribution (see results in section 4.2.1).

3.5.3 Sensitivity due to parameter uncertainty (Monte-Carlo analysis)

Additionally, sensitivity due to uncertainty in the model parameters is expected. We performed a Monte-Carlo-type analysis similar to the Great-ER model (Koormann et al. 2006) to estimate the individual and combined effect of parameter uncertainty on the resulting concentrations. The model is run several hundred times, and for each time, the model varies the value of a parameter randomly, within user defined boundaries. If run many times (at least 500 times is

recommended), the model covers a wide range of possible combinations of values for each parameter. The results can then be aggregated into statistical indices of means, minimum, maximum, and 95th percentile confidence intervals.

Table 5: Parameters used for the calculation of the source and fate of Carbamazepine

	Units	Carbamazepine
Total consumption (Canada) [a]	kg/yr	22443
Per capita consumption (CAN) [a],[b]	milligrams/cap.d	1.86
Total consumption (US) [c]	kg/yr	137300
Per capita consumption (US) [c],[b]	milligrams/cap.d	1.26
Metabolic loss [d]	%	83.4
Reduced through 1) Primary treatment [d]	%	0
Reduced trough 1a) Lagoon [e]	%	0
Reduced through 2) Activated Sludge [d]	%	9
Reduced through 2a) Trickling Filter [e]	%	0
Reduced through 3) Tertiary treatment [d]	%	9
Degradation constant [d]	day^{-1}	0.0088
PNEC aquatic [f],[g]	µg/L	0.5
PNEC human [f]	µg/L	0.32

a) IMS Brogan (2006a, b), b) United States Census Bureau (2013), c) Zhang and Geißen (2010), d) Cunningham et al. (2010), e) assumed, f) Smit and Wuijts (2012), g) Kase et al. (2011)

As appropriate monitoring data of spatio-temporal variations of substance usage and of the behaviour of the substance in the environment are lacking, a comprehensive parameter uncertainty assessment has not been conducted. Instead, the uncertainties of input parameters have been estimated by entering a range (given in percent) within which the value can deviate from the given value. The model then generates new random values within the defined boundaries and uses them as input for the Monte-Carlo model runs. For example, if a certain

chemical input is 50 mg/cap/day, and the variation is estimated at 30 percent, then for each model run the simulator first generates a random number between 35 and 65 mg/cap/day. The likelihood that the simulator selects values at both ends of the spectrum is increasingly reduced, implemented as a triangulate probability distribution (also known as three-point-estimation[7]).

The percentage of variation defined by the user is currently applied to the per capita consumption, the discharge, and the in stream-decay factor (*k*). The results of the different simulations are shown in Figure 14 in section 4.2.2.

3.5.4 Distribution of concentrations

Histograms and cumulative probability distributions are commonly used tools to evaluate measured concentrations in rivers. For our validation we calculated cumulative distributions for a number of measurements for Carbamazepine as found in the literature and as calculated from our model.

In total, we analyzed 373 reported samples from 19 different studies, including: Metcalfe et al. (2003), Miao and Metcalfe (2003), Brun et al. (2006), Hua et al. (2006), Lissemore et al. (2006), Lajeunesse and Gagnon (2007), MacLeod et al. (2007), Yargeau et al. (2007), Viglino et al. (2008), Garcia-Ac et al. (2009), Viglino et al. (2009), Li et al. (2010), Rahman et al. (2010), Tabe et al. (2010), Waiser et al. (2011). We plotted the concentrations as cumulative frequency curves including non-detects (see section 4.2.3).

3.5.5 Point-by-point validation

Finally, we used point-by-point validation (PPV) to compare the simulated concentrations from our model to the observed concentrations measured at specific point locations in the river network. Ideally, the on-the-ground observations should be collected following a specific and structured monitoring campaign (see section 5.2 for recommendations). In this report, however, we only use observed concentrations from two Carbamazepine studies, one peer-reviewed study by Lajeunesse and Gagnon (2007) and one Master Thesis from the University of Waterloo (Kormos 2007).

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[7] See also: **http://en.m.wikipedia.org/wiki/Three-point_estimation**

4. Results

4.1 HydroROUT discharge validation

4.1.1 Validation of long-term average annual flows

Figure 10 shows the results of the comparison of long-term annual flows as recorded at the 57 "most reliable" HYDAT stream gauges (for selection criteria see 3.1.1 above) and as provided by the HydroROUT model. The linear regression model suggests a very high correlation and indicates that the HydroROUT model is able to account for 98.2% of the variation in the observed data (coefficient: 1.05; residual standard error: 0.244; results are statistically significant at the 95% confidence level).

Additional validation sets and results incorporating a larger number of HYDAT gauging stations are available in the Appendix (Table A-2 and Figure A-6), including some discussion.
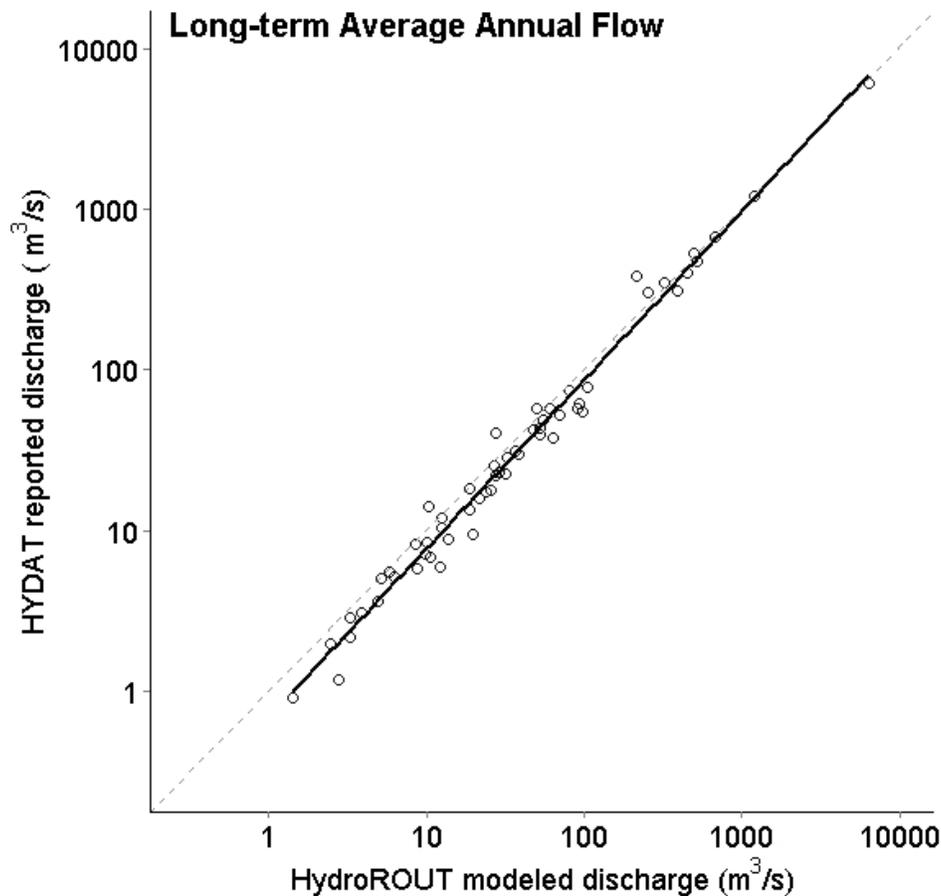
Figure 10: Scatterplot of observed and modeled long-term average flow

4.1.2 Q90-Month as a proxy for daily Q90 values

Due to limitations in the temporal resolution of the underlying global hydrological runoff model WaterGAP (see section 3.1 above), Q90-Month (i.e. the lowest long-term average monthly flow) is proposed as a substitute for the commonly used daily Q90 low flow index. In order to assess the adequacy of this substitution, we tested the correlation between Q90-Month and (daily) Q90 for the "most reliable" 57 HYDAT stations. Figure 11 shows that a very good correspondence between the two indicators exists, and Q90-Month is able to account for 96.7% of the variation in the (daily) Q90 values (coefficient: 1.123; residual standard error: 0.4461; results are statistically significant at the 95% confidence level).

However, Q90-Month tends to systematically overestimate Q90, in particular for very small streams. This means, with respect to fate modeling, that low flow assessments based on Q90-Month are likely underestimating substance concentrations and the risk of contamination as compared to analyses using daily Q90.
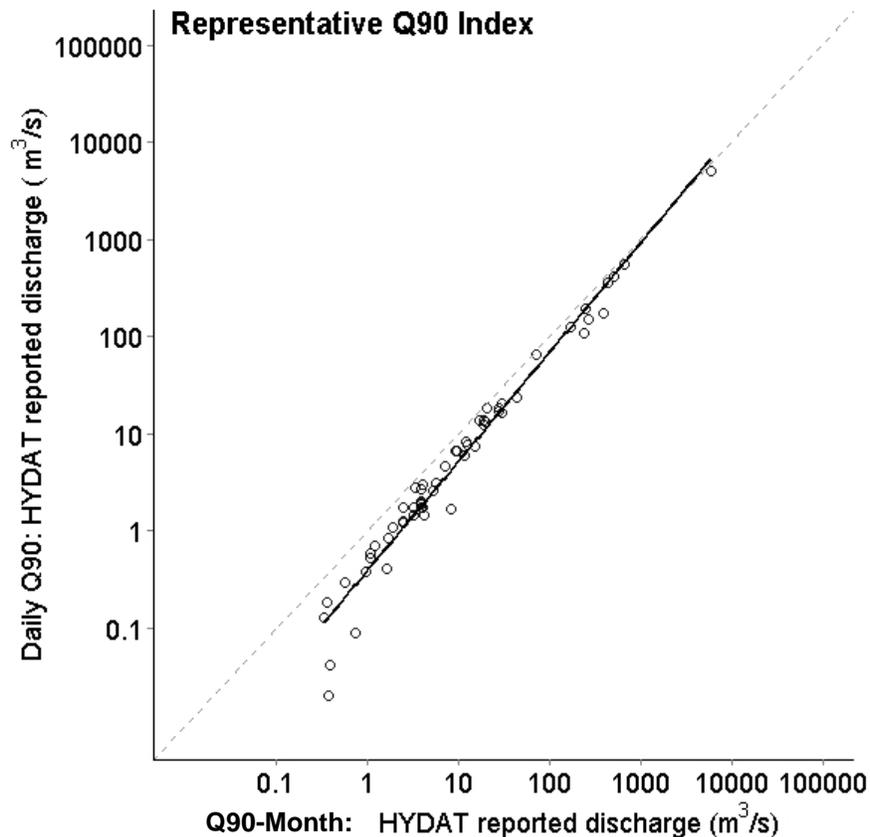
Figure 11: Scatterplot for Q90-Month and Q90 calculated from observed discharge data

4.1.3 Validation of low flows (Q90-Month)

Figure 12 shows the results of the comparison between the observed and modeled low flow index Q90-Month for the "most reliable" 57 HYDAT stations. The linear regression model confirms a high correlation and indicates that the HydroROUT model is able to account for 90.2% of the variation in the observed data (coefficient: 1.043; residual standard error: 0.6743; results are statistically significant at the 95% confidence level). Additional validation sets and results incorporating a larger number of HYDAT gauging stations are available in the Appendix (Table A-1 and Figure A-5), including some discussion.

As expected, the associated error for low flow conditions is higher than for long-term average discharges. Differences between modelled and reported low flows can vary by up to one order of magnitude, especially for smaller rivers. This is likely caused by the more extreme nature of low flow conditions as well as the potential for significant anthropogenic influences in terms of flow regulation that are not adequately represented in the hydrological model. Accordingly, the uncertainty for predicting contaminant concentrations for low flow conditions is increasing. Nevertheless, in terms of contamination modeling this range of error may still be tolerable for the purpose of general screening and hot spot analyses. Also, switching to the updated version of the underlying global runoff model may improve the results.
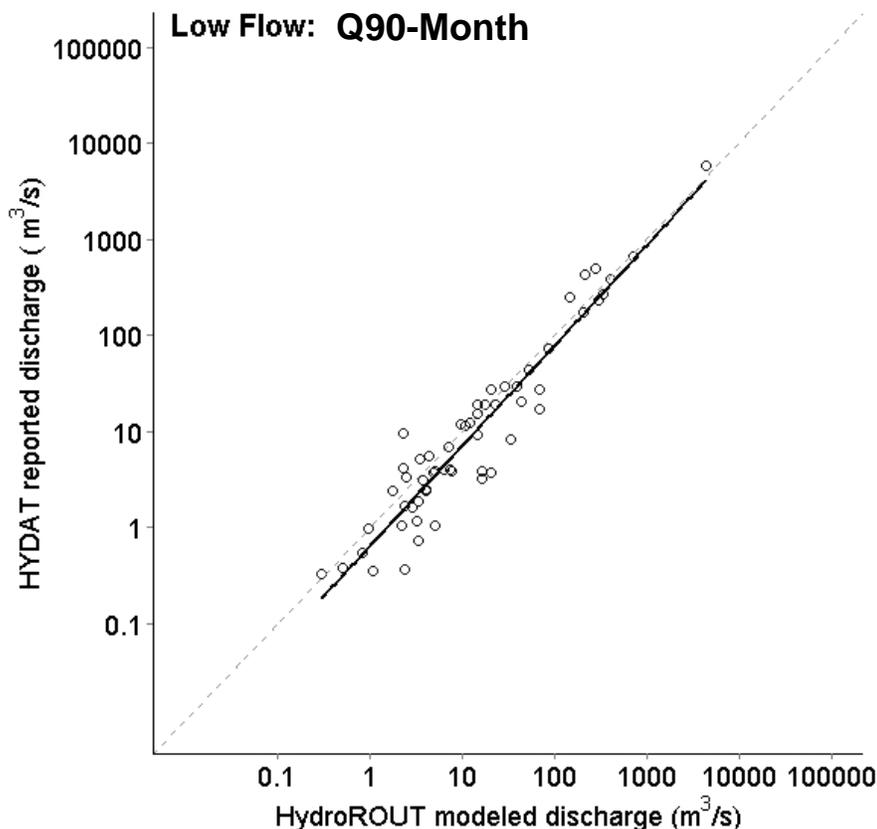
Figure 12: Scatterplot for observed and modeled Q90-Month low flow values

4.1.4 Comparison of long-term average monthly flows

In the Annex of this report are four figures (A-1 to A-4) depicting comparisons of flow regimes for long-term average monthly flows derived from observed HYDAT station data and simulated by the HydroROUT model. The Nash–Sutcliffe model efficiency (NSE) was used as a measure of the predictive power of the HydroROUT model. This analysis was executed using the HydroGOF package[8] in R. NSE values can range from minus infinity to 1, with 1 being the best value, and negative values indicating a less than random fit.

Based on these NSE values, we prescribed ratings following (with slight modifications) suggestions by Moriasi and Arnold (2007, p. 891) for examining river flow data with a monthly time step (Table 6). Although the resulting NSE coefficients are low or unsatisfactory in many cases, these results need careful interpretation. In particular, the NSE coefficient is not very suitable for capturing situations where a temporal shift in discharge regimes exists while the overall shape of the curve is similar (see Figure A-4). Such shifts are often observed in large scale models for high latitudes, where snowmelt process are predominant, and temporal shifts of one or two months due to inadequate representation of daily temperature fluctuations are common. The important measure for our contamination risk assessment model, i.e. the magnitude of the low flow index Q90-Month, may still be represented reasonably well despite this temporal shift in the flow regime.

Table 6: NSE rating summary for 57 selected HYDAT stations

NSE rating	Range	Count
Very Good	1.00 ≥ NSE >0.75	2
Good	0.75 ≥ NSE > 0.65	3
Satisfactory	0.65 ≥ NSE > 0.50	5
Inconclusive	0.50 ≥ NSE ≥ 0	14
Unsatisfactory	NSE < 0	33

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[8] **http://cran.r-project.org/web/packages/hydroGOF/hydroGOF.pdf**

4.2 Mass balance validation: case study Carbamazepine

4.2.1 Sensitivity due to removal process uncertainty

Figure 13 illustrates the effect of removal processes on the distribution of Carbamazepine concentrations in the river network. If the process of metabolism in human population is introduced (with 83.4% of all input being removed; see Table 5), the resulting concentrations change significantly. The uncertainty around this removal range, however, is currently unknown. The additional removal in the treatment process of WWTPs has little impact on the concentration of Carbamazepine. Most large treatment plants do not have secondary or tertiary treatment, and those that have, remove only 9% of the load (Table 5).

Removal during lake routing has a noticeable effect on concentrations, and the applied area threshold is important. Since the total load is removed completely, strong local reductions of concentrations occur after lakes, as compared to no lake removal where the entire load is passed downstream. Finally, in-river decay has very little effect on Carbamazepine concentrations, because of its very long half-life in the environment (~70 days). The lines for in-river decay and lake routing (100) are therefore barely distinguishable in the graph. All removal processes but metabolization have little effect on the 95th percentile concentration.
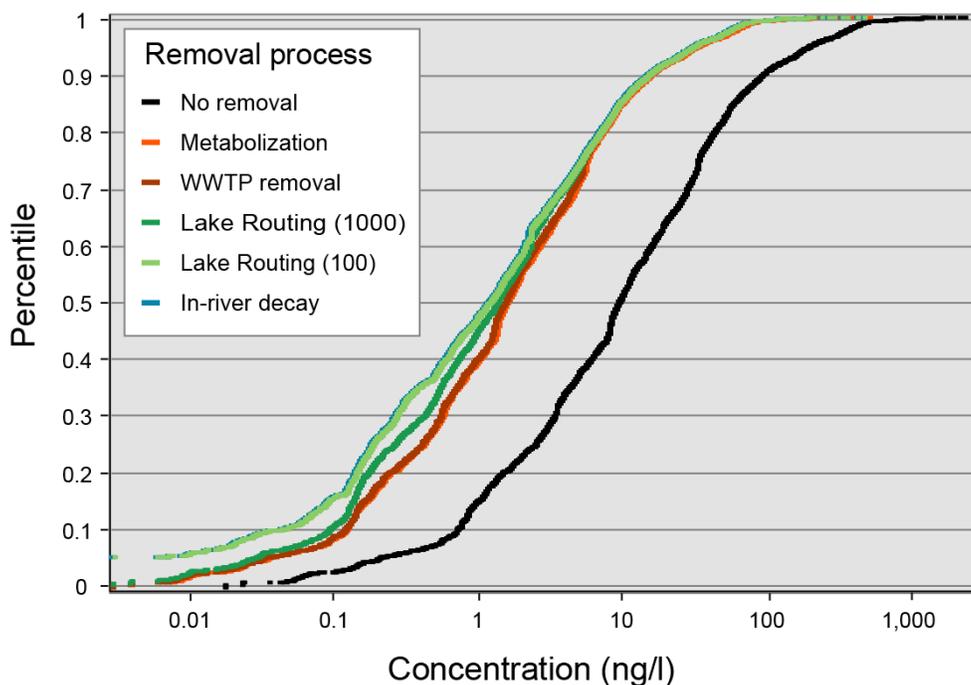
Figure 13: Effect of various removal mechanisms on the simulated concentrations of Carbamezapine. The removal processes are added sequentially in the order shown in the legend. Lake surface area thresholds of 100 km^2 and 1000 km^2 are applied at which the entire load is assumed to be removed.

4.2.2 Sensitivity due to parameter uncertainty

The input parameters of our model are subject to uncertainty. For this study, we assumed that uncertainty in drug usage, discharge, and in-river decay had the most influence on resulting concentrations. We used the simple assumption that each of the three parameters can vary by up to 50% of its given value. We then conducted a sensitivity analysis performing a Monte-Carlo analysis. The results are shown in Figure 14 and illustrate the concentration ranges (min, max, average) for average flow conditions, and for low flow conditions.

The concentrations between average flow and low flow conditions can vary significantly, up to a factor of 2-3, with somewhat smaller differences for lower concentrations. This may be explained by large rivers (which typically show lower concentrations) being less prone to changes between average and low flow conditions, whereas smaller rivers (typically showing the highest concentrations) are more sensitive to river flow changes. Importantly, the range in concentrations that is additionally introduced due to parameter uncertainty is in the same order of magnitude or even larger than the difference between average and low flow conditions.
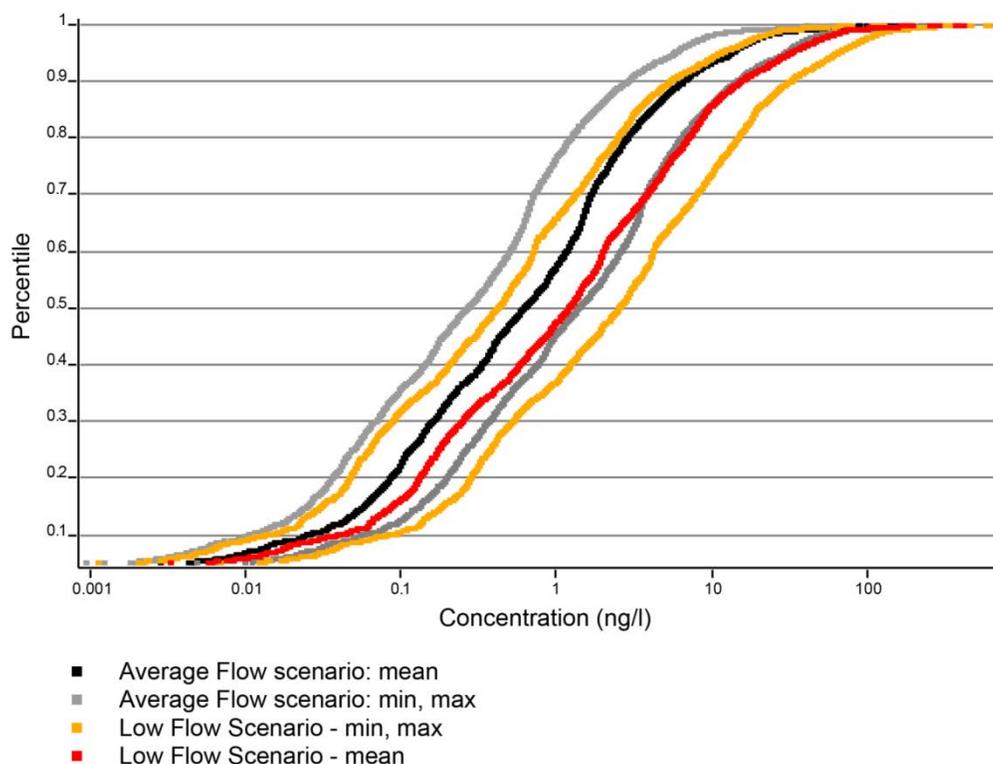
Figure 14: Cumulative frequency plot with minimum, maximum, and average concentrations of Carbamazepine. Black and grey colors represent average flow conditions; red and orange represent low flow conditions. Ranges are computed based on 500 Monte-Carlo simulations with random variation of parameters up to 50% for the parameters: substance usage, river discharge, and in-stream decay. The model settings for this analysis are displayed in Figure 8).

4.2.3 Comparison of cumulative probability plots

A quantitative comparison between simulated and observed Carbamazepine concentrations is shown in Figure 15. We used the same model simulations as before, and added the observed Carbamazepine concentrations from our literature review to the plot. Roughly 52% of the samples across the 19 studies analysed detected Carbamazepine in surface waters (lakes and bays were excluded). The observed concentrations plotted against the simulated ones with relatively good agreement. The observed concentrations fall within the range of both average and low flow simulated concentrations. The 95th percentile concentrations for Carbamazepine were 13 ng/l (min 6 - max 29), 31 ng/l (11-65) and 85 ng/l under simulated average flow conditions, low flow conditions and for observed concentrations, respectively.

The difference between observed and simulated 95th percentile concentrations can be attributed partly to the limited availability of data points across different river sizes, but more likely also to the fact that measurements are generally biased towards collecting samples from surface waters with high concentrations, such as downstream of wastewater treatment plants (Hannah et al. 2009). Furthermore, almost no study reports the river flow at the time of measurement, which complicated the comparison further.
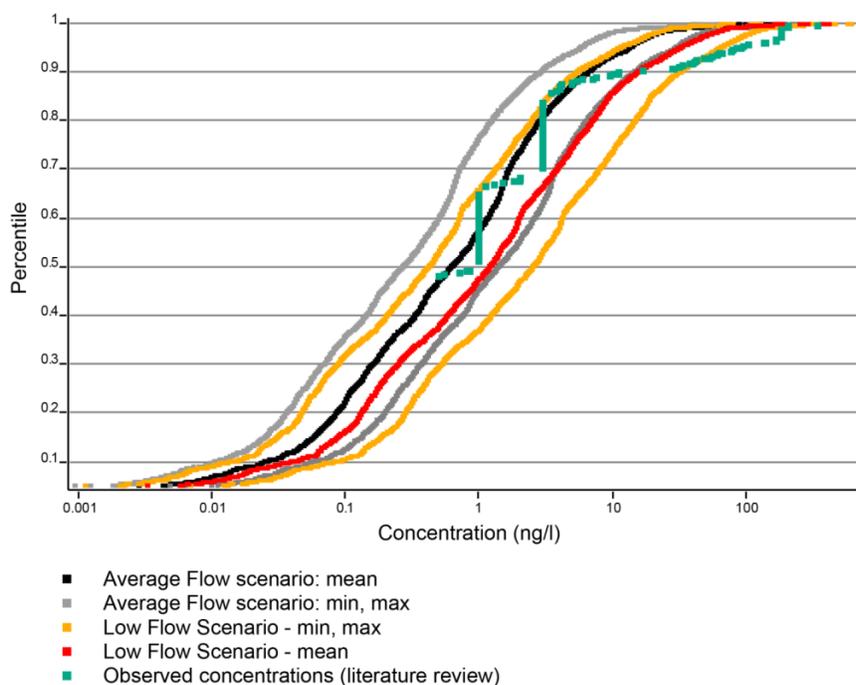
Figure 15: Cumulative frequency plot with minimum, maximum, and average concentrations of Carbamazepine (see Figure 14 for explanations). Also plotted are observed concentrations for Carbamezapine in Canadian surface waters, compiled from 19 studies which analyzed 373 samples for the presence of Carbamezapine. Cumulatively, Carbamezapine was detected in 52% of the samples analysed (non-detects are included in the graph).

4.2.4 Point-by-point validations

Case 1: St. Lawrence River at Montreal

In order to conduct a point-by-point validation, we used point locations provided by Lajeunesse and Gagnon (2007), who measured upstream and at distances of up to 8km downstream of the Montreal wastewater treatment plant in the St. Lawrence River. Montreal's WWTP is only equipped with primary treatment technology. As a result, little PPCPs are removed due to the treatment process (see also Gagnon and Lajeunesse, 2012). The measurements of Lajeunesse and Gagnon (2007) provided for low flow conditions indicate that the Montreal WWTP has a large effect on the surface water Carbamazepine concentrations, which is also represented in our model by the sudden increase of concentrations measured in the St. Lawrence River (Table 7).

Table 7: Simulated and observed Carbamazepine concentrations (ng/l) in the St. Lawrence River near Montreal

	0.5 km upstream WWTP	0.5 km downstream WWTP	2.5 km downstream WWTP	4.5 km downstream WWTP	8 km downstream WWTP*
HydroROUT simulated	0.77	1.7	1.7	1.7	2.0
Lajeunesse and Gagnon (2007)	0.8	7.4	5	4	3.5

* Note: This location includes the load from two additional treatment plants and from the Miles Iles River

The comparison with the study by Lajeunesse and Gagnon (2007) needs careful interpretation. The measured river flow at the day of observation was 8340 m³/s according to HYDAT at Station St. Lawrence/Lasalle (Station ID: 020A016), whereas HydroROUT's Q90-Month index for low flow conditions indicates 7776 m³/s, i.e. nearly 10% lower than the measured value. Higher concentrations are thus expected from HydroROUT, yet simulated concentrations are roughly 40% lower than observed. On the other hand, Lajeunesse and Gagnon (2007) do not provide measured effluent concentrations from the WWTP for the observation date. Although little inter-annual variation may be expected, the same study references two effluent measurements at the same time of the year that differ by a factor of seven (656 ng/l on 27 April 2005 compared to 91 ng/l on 26 April 2006). Since we do not know the effluent concentrations on the observation day, we cannot be sure whether the given in-river concentrations are on the high or low end of the spectrum.

Finally, it should be noted that literature studies in general tend to rely on measurements made directly in the sewage effluent or immediately downstream of a treatment plant, likely within the discharge plume of the WWTP. Our current model cannot represent concentrations at specific points within the mixing zone since it assumes full mixing of the wastewater parcel upon release. Therefore, simulated concentrations might be smaller than those reported in literature.

Case 2: Grand River at Kitchener

A study by Kormos (2007) measured and analysed raw surface water concentrations of Carbamazepine at two drinking water plants in the Grand River Basin, Ontario (see Figure 16) and included detailed river discharge at the time of measurement (Table 8). The comparison between observed and simulated flow showed good overall agreement between HYDAT's reported low and average flow values with our model (Table 9) although the flow is simulated notably higher than observed at Facility B. We then compared simulated concentrations under low flow conditions with predicted environmental concentrations from our model (Table 10). Despite the differences in modelled discharge for one of the stations, we still observed a good agreement between

Figure 16: Location of measurement stations (Facility A and B). Map taken from (Kormos 2007).

observed and simulated concentrations. Note that the variability in monthly loading was quite high, ranging from 441g to 855g for Facility A, and 1205g to 2757g (excluding the outliers in August 2005) for Facility B.

Table 8: Raw surface water concentrations of Carbamazepine (ng/l) and mean daily flows (m^3/s) at two drinking water stations at the Grand River, Ontario (Kormos 2007; see p. 123 and 152). Flow measurements from HYDAT stations; orange shading indicates measurements in low flow periods (as used in Table 10). Numbers in parenthesis are considered outliers.

Year Day/Month	'05 5/4	'05 3/5	'05 7/6	'05 5/7	'05 2/8	'05 6/9	'05 4/10	'05 15/11	'05 6/12	'06 3/1	'06 7/2	'06 7/3
Facility A												
Sample 1	2.8	7.6	25	27	22	16	19	24	11	7.1	3.2	12
Sample 2	2.7	7.1	22	28	20	17	18	22	11	8.5	2.8	12
Observed flow	85	30	15	10	11	10	13	10	25	30	65	15
Facility B												
Sample 1	7.9	14	52	72	(1015)	51	33	42	18	19	8.2	27
Sample 2	7.6	14	53	67	(961)	52	31	43	21	16	7.9	29
Observed flow	140	50	20	15	13	14	15	15	30	48	95	25

Table 9: Comparison between observed and simulated long-term flow (m^3/s) at two drinking water stations at the Grand River, Ontario. Observed values calculated from HYDAT gauges for the time period 1961-90.

	Observed average	Simulated average	Observed Q90-Month	Simulated Q90-Month
Facility A	**37.9**	**42.3**	**14.4**	**11.4**
Facility B	**58.1**	**91.0**	**20.1**	**25.1**

Table 10: Comparison between observed and simulated Carbamazepine concentrations (ng/l) at two drinking water stations at the Grand River, Ontario, for low flow conditions. The concentration for the "observed Q90-Month" flow was approximated by taking the median of the shaded cells in Table 8 (months of lowest flow) for each sample, and then calculating the average for each facility. SD = Standard Deviation.

	Observed Q90-Month	Simulated Q90-Month	*SD*
Facility A	**21.0**	**25.8**	*14.3*
Facility B	**51.5**	**48**	*7.8*

4.3 Dilution factors

4.3.1 Cumulative frequency plot of dilution factors
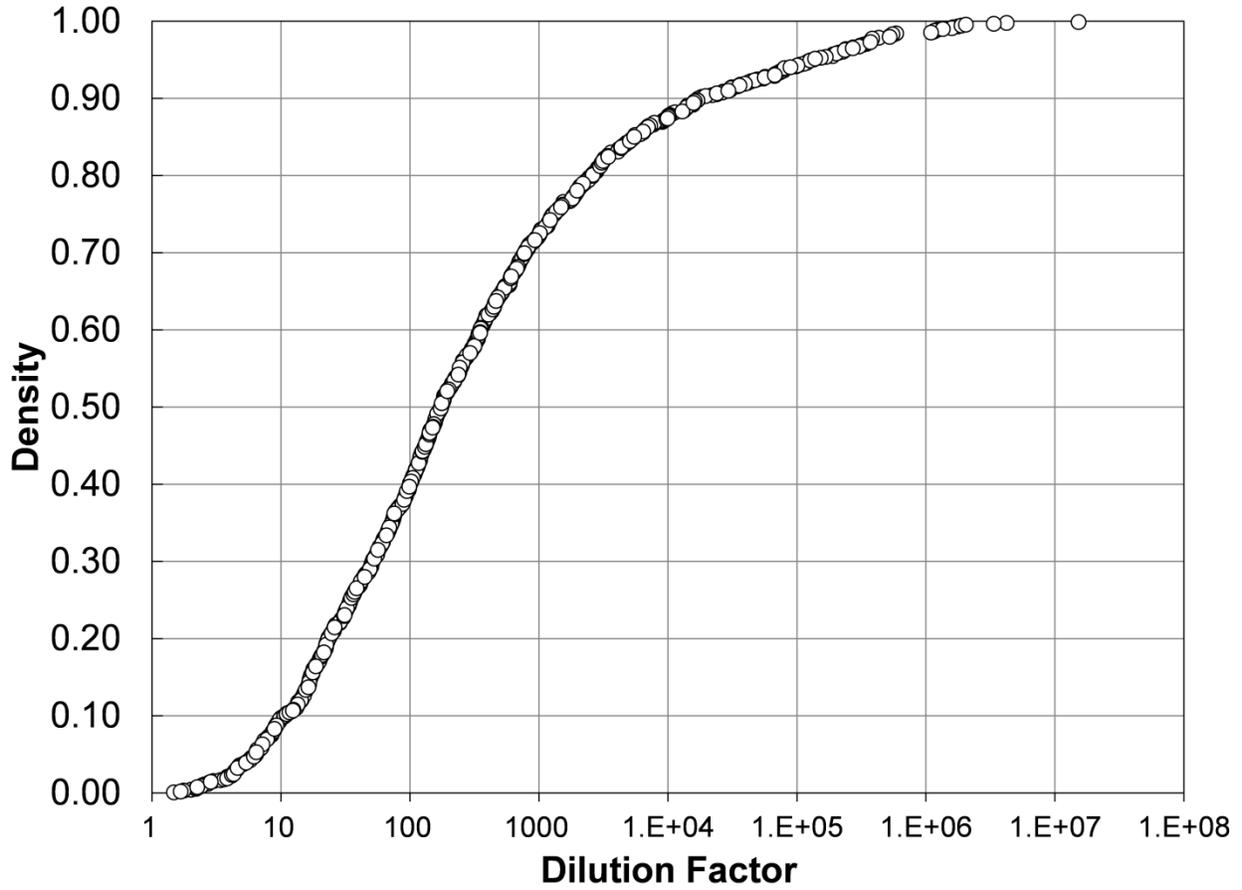
Figure 17: Cumulative frequency plot of dilution factors. A total of 888 WWTPs were included; WWTPs that discharge into lakes, or discharge seasonally were excluded.

4.3.2 Map of dilution factors
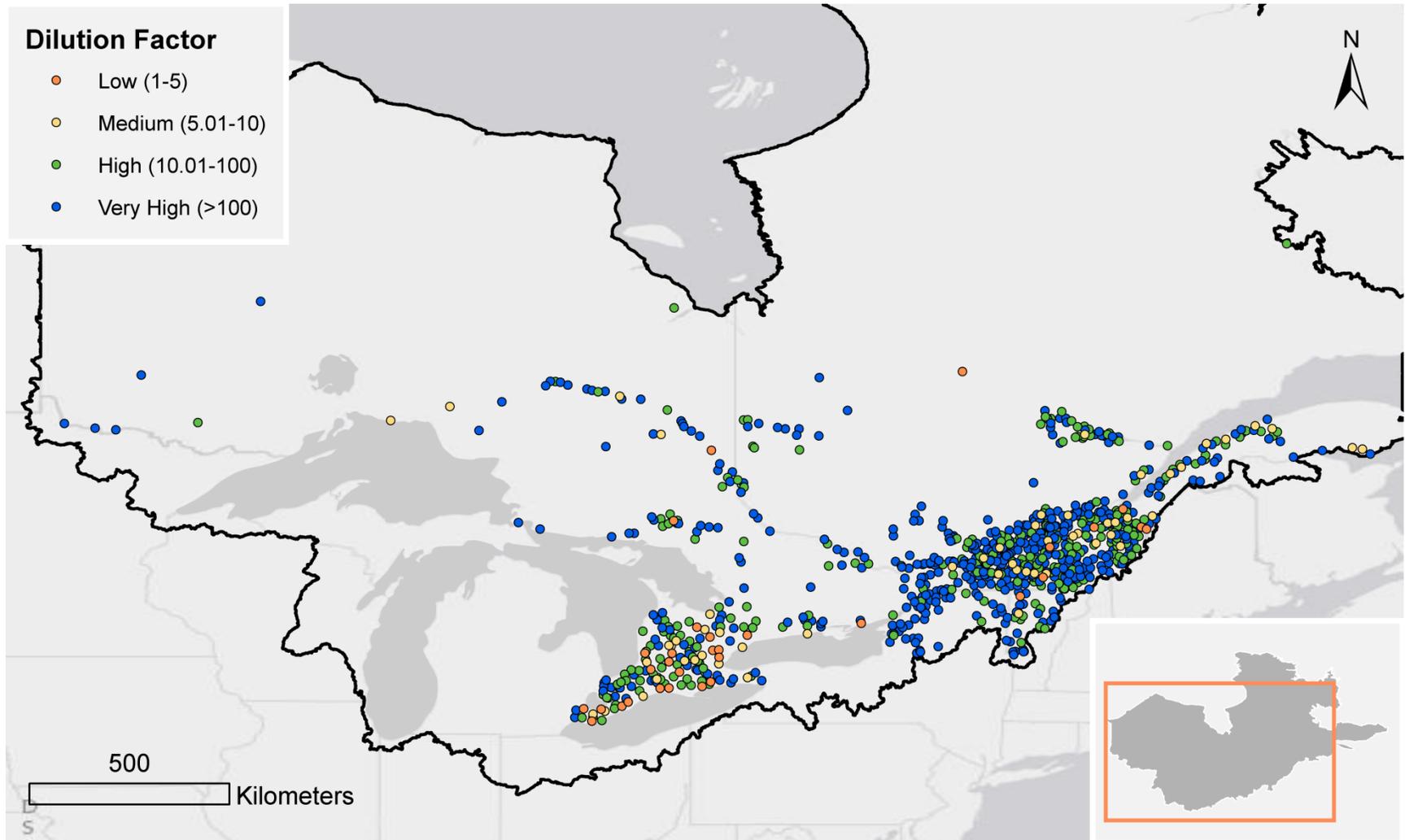
Figure 18: Map of dilution factors under low flow conditions (Q90-Month)

4.4 Percent wastewater
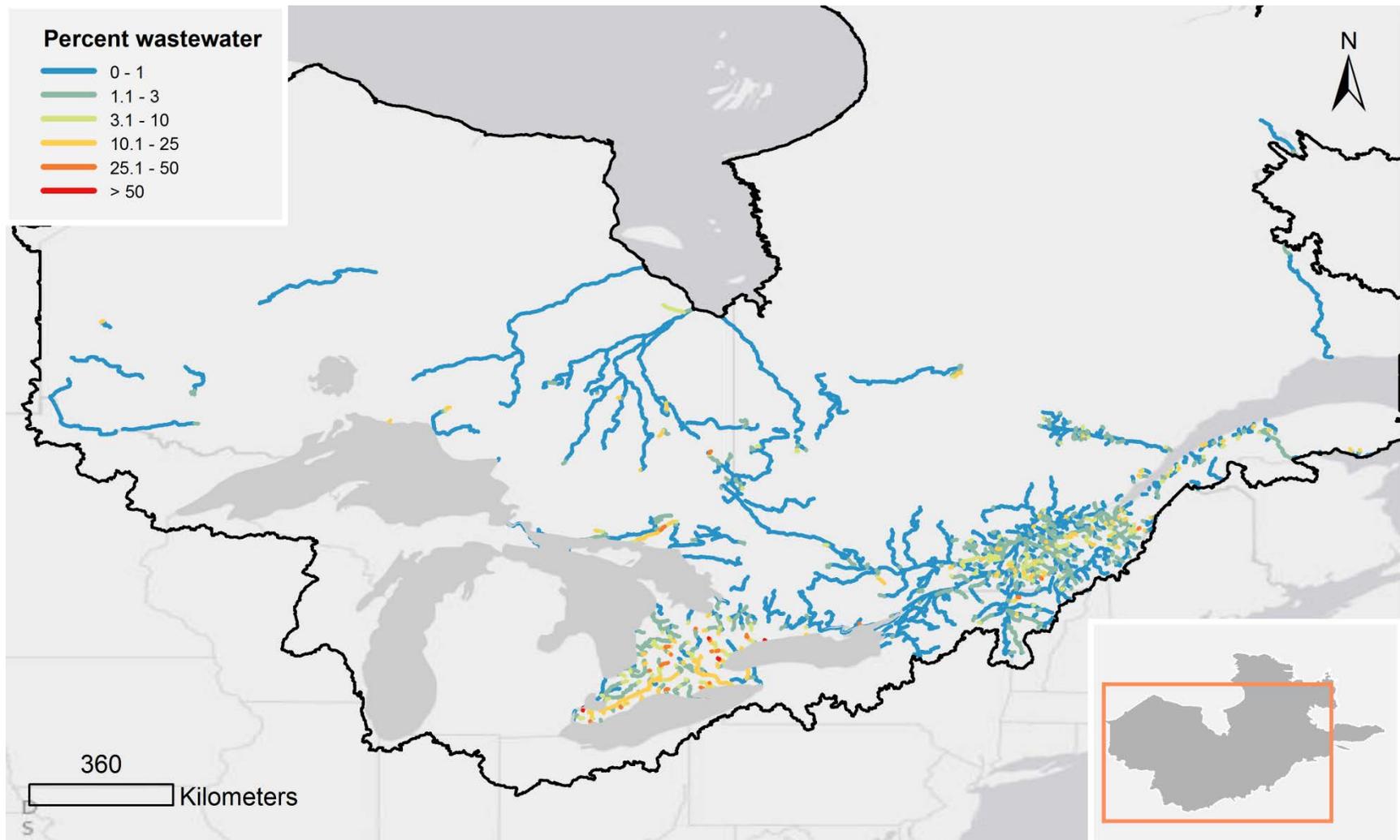
Figure 19: Percentage of wastewater in river course under low flow conditions (Q90-Month)

4.5 Carbamazepine concentration in the Saint Lawrence River
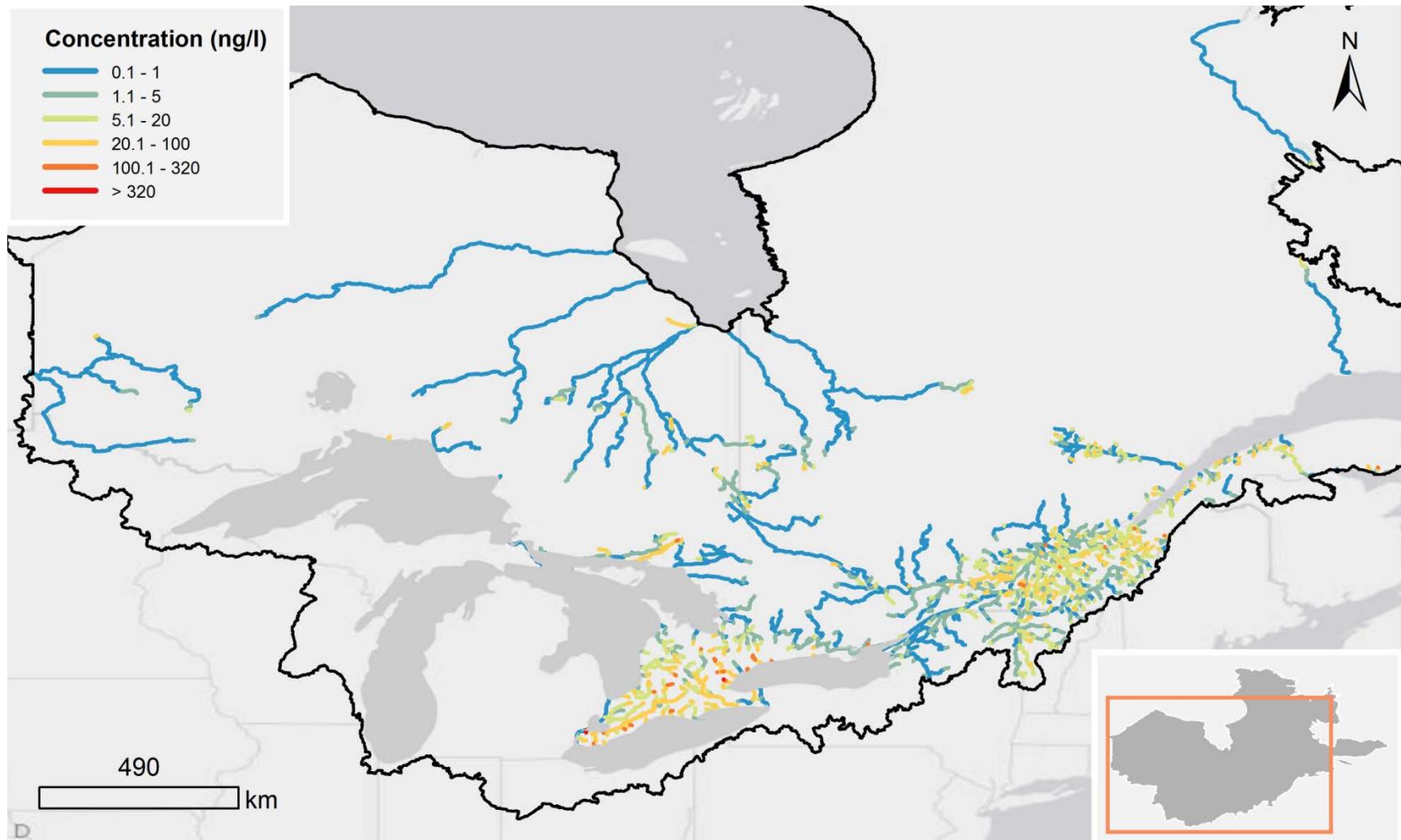
Figure 20: Simulated Carbamazepine concentrations under low flow conditions (Q90-Month)

4.6 Lists of rivers with high Carbamazepine concentrations and percentage of wastewater

Tables 11 and 12 present rankings of our model results in terms of the most severely affected rivers for Carbamazepine concentrations and for the percentage of wastewater. Similar rankings are found in both concentration and percentage tables since effluent volume and population served (and therefore load) are highly correlated. The differences in ranking can be explained by the different treatment processes of the wastewater treatment plants located along the river course.

It should be noted that the most extreme concentrations and percentages of wastewater were simulated in the model for very small and unnamed tributaries. Despite additional efforts, our current status of river names is not complete for small rivers, yet we believe that the most important ones have been included.

4.6.1 Carbamazepine concentration in rivers

Table 11: Maximum and mean Carbamazepine concentrations (ng/l) in river courses under low flow conditions (Q90-Month)

| No.	Name	Max. concentration (ng/l)	Mean concentration (ng/l)	Province
1	Credit River	232	50	ON
2	Don River	123	119	ON
3	Blanche River	95	9	ON
4	Maitland River	72	17	ON
5	Thames (North Thames)	70	48	ON
6	Grand River	67	30	ON
7	Ausable River	48	13	ON
8	Rivière Bécancour	35	15	QC
9	Rivière du Nord	34	22	QC
10	Rivière Champlain	21	10	QC
11	Yamaska	20	11	QC
12	Rivière Doncaster	20	6	QC
13	Mississippi River	18	10	ON
14	Rivière Châteauguay	15	2	QC
15	Rivière L'Assomption	14	5	QC
	Overall maximum (small tributary)	*446*		

4.6.2 Percent wastewater in river courses

Table 12: Percentage of wastewater in river courses under low flow conditions (Q90-Month)

No.	Name	Wastewater % (max)	Wastewater % (mean)	Province
1	Credit River	62	14	ON
2	Blanche River	38	4	ON
3	Maitland River	29	7	ON
4	Thames (North Thames)	21	16	ON
5	Grand River	19	10	ON
6	Don River	18	17	ON
7	Mississippi River	17	9	ON
8	Ausable River	13	3	ON
9	Yamaska	9	5	QC
10	Rivière du Nord	9	6	QC
11	Rivière Bécancour	8	4	QC
12	Riviere des Envies	7	2	QC
13	Rivière Doncaster	7	2	QC
14	Rivière L'Assomption	4	2	QC
15	Rivière Champlain	4	2	QC
	Overall maximum (small tributary)	*71*		

4.7 Risk for drinking water sources

An example for a simple visual risk assessment is shown in Figure 21 below. By superimposing the contaminant indicator with the locations of assumed drinking water intakes, a visual inspection can point to potential locations at risk from wastewater contaminants. For the entire province of Ontario, 77 (out of 122) drinking water intakes were associated with rivers affected by WWTP effluents. In future studies, such evaluations could be automated by directly comparing the concentration at the drinking water intake location with the simulated concentrations.

Figure 21: Sources of drinking water and percentage of wastewater in river courses

It should be noted, however, that although the locations of drinking water treatment plants were available as point coordinates, the actual location of water intake points could not be confirmed from the available data in more detail than assigning it to the nearest water body. There may be cases in which a drinking water treatment plant collects water from a distant location using pipes and other infrastructure. Considering this issue, the location of drinking water intake points is only considered to be a best-guess estimate. Furthermore, the treatment techniques may vary from site to site, removing different levels of contaminants from the intake water. These data uncertainties should be considered before highlighting water intake points at risk of contaminant exposure.

5.   Discussion

5.1 Model uncertainties and sensitivity

As any model, the presented discharge and fate model shows a variety of inherent uncertainties related to process descriptions and parameter settings. A particular problem for large-scale models is the often limited availability or unknown quality of input data. In the case of fate modeling, uncertainties can be largely attributed either to the hydrological flow simulations or to the representation of chemical inputs and decay.

For the modeling of large-scale runoff, important factors affecting the accuracy of the routed discharge include, but are not limited to, errors in the routing process (e.g., related to flow velocity, channel geometry, flow attenuation) and errors due to inadequately represented flow regulation structures. Human controlled flow regulation features such as dams and reservoirs are common in the study area, possibly causing a misrepresentation in particular of low flow conditions. Also, errors in the routing of diverging (bifurcating) river channels (which may converge again further downstream) can cause significant inaccuracies in HydroROUT as the model is currently unable to represent this situation.

A new discharge map is currently in development, but, unfortunately, could not be included in the presented analysis. We expect completion of this layer by the end of 2013. Due to improvements in the underlying global runoff model (finer resolution, variable flow velocity routing, and new dam management algorithm), we are hopeful that significant improvements can be realized by including this new input data.

In the current model version, we use variable flow velocity based on Allen et al. (1994). This approach is very simplistic (see section 3.4.7 above) and affects, among others, the time available for in-stream decay. This method is subject to further verification and uncertainty analysis.

The simple lake routing model that has been implemented in the model assumes either complete elimination or complete passage of chemicals in lakes. This simplification, obviously, is unrealistic in cases where (medium sized) lakes are passing some concentrations downstream. This error could be reduced by using a better lake routing scheme. In order to do so, lakes could be modeled as a series of 'stirred reactors'. This approach has already been implemented in the model, but has not been used due to a lack of data describing lake volumes. As a coarse-level approximation, lake volumes could be estimated based on surrounding topography and lake properties (Hollister and Milstead 2010).

To assess the model sensitivity related to parameter uncertainty, the Monte-Carlo simulation module is currently based on simplified assumptions to generate combinations of parameter sets.

We applied a triangular probability distribution instead of more realistic functions such as normal or log-normal distributions. For parameters such as discharge or flow velocity, actual error distributions could be used to estimate better probability curves to be used in the Monte-Carlo simulations (based on data from section 4.1 above). Typically, a log-normal distribution is used for discharge, but the exact shape of the distribution needs to be defined statistically, which has not been attempted yet. We believe, however, that better implementation of uncertainty can further improve the confidence in the model outputs.

The following additional limitations of the fate model are known but cannot be further resolved within the scope of this project. Note, however, that these limitations and simplifications are not expected to dominate the overall performance and quality of the large-scale model.

- **Steady-state routing mechanism**

  Steady-state routing was assumed, which means that there is no temporal variation in the substance concentrations of a river. Discharge remains constant within each steady-state model run (Monte-Carlo simulation); i.e., there is no dynamic flow routing implemented.

- **Constant chemical emissions**

  We have not addressed the temporal variation in product consumption and associated chemical emissions. Consumption may vary inter-annually or seasonally, may change between different days of the week, or may follow diurnal fluctuations (Kormos 2007). These patterns in product consumption are currently disregarded since such information is typically not available. More insight into the variation of specific chemicals could improve the settings of the sensitivity analysis and could allow for more realistic results.

- **Full mixing within the river reach**

  Inflow from WWTPs is assumed to occur from the most upstream point of the river reach even if the treatment plant is located close to the end of the river reach. Furthermore, no variation of concentration is calculated within a single river reach. Reaches are in average approximately 3 km long (but vary in size) and a uniform concentration along each reach is assumed.

- **WWTPs that discharge directly into lakes**

  If a treatment plant discharges directly into a lake, or is located within 2 km upstream of a lake, we assume complete instantaneous mixing with the entire lake volume; i.e., no contaminant plume can be modelled.

- **Unaccounted contaminant input**

  The contaminant fate model does currently not include input from atmospheric deposition, erosion or surface runoff, or from non-treated wastewater. The latter could be a significant contributor since the connection of the population to sewage treatment plants is incomplete and can reach as low as 70% in some regions.

- **Topological misrepresentations**

  The topological concept of HydroSHEDS is based on a single channel system; i.e., bifurcations are not represented in the model by design. In Quebec and Ontario, such situations occur, for example, around the island of Montreal, and there may be various other cases. The bifurcation areas are inadequately represented; in particular, the distribution of stream flow among the individual channels is unknown. Affected river reaches should either be excluded or be verified to ensure that their properties are realistic (i.e., average and low flow values).

5.2 Uncertainties in mass balance validation

We conducted point-by-point validation as well as comparisons of concentration distributions based on reported values from the literature. However, a number of shortcomings should be pointed out that apply to both of these approaches:

- Most studies that we found focused on measurements of contaminant concentrations in WWTP effluents and rarely measured concentrations in different sections of a river (Hannah et al., 2009).

- Many studies do not report an exact location, which makes it difficult to geo-locate the samples in the river network.

- The river flow at the time of concentration measurement, or the date of measurement in order to search for flow quantities in existing records, is almost never available, which complicates the evaluation of the performance of the mass balance model.

- Due to the fact that studies often report on measurements conducted in highly polluted rivers (e.g., immediately downstream of wastewater treatment plants) the cumulative frequencies of concentrations are artificially biased towards higher values. In contrast, our model includes all river reaches independent of their potential contamination.

A possible improvement to the validation methodology could be achieved by comparing cumulative probability plots for specific regions, with simulated and reported concentrations from similar river reaches.

5.3 Possible improvements of model performance and validation

Based on the results presented, we believe that the model is capable of realistically estimating in-river concentrations of contaminants for the purpose of screening for problematic chemicals, especially considering that a typical goal of such models is to simulate concentrations that are within an order of magnitude of the measured concentrations. If greater certainty about the model performance is needed, we suggest that a small measurement campaign be conducted that would result in a set of in-river measurements of specific substances. This data would be used in combination with modelling results to assess with greater confidence the suitability of the mass balance model beyond what is currently possible. It is envisioned that such a campaign would include the following attributes:

- The chemical marker chosen would be one that: (1) is primarily released to surface waters via sewage treatment plants; (2) is readily detectable in rivers of various sizes; and (3) demonstrates low potential to be removed in surface waters due to various removal mechanisms (e.g., biodegradation, photolysis, hydrolysis and sorption).

- Approximately 100 samples would be taken across a wide range of river size classes at locations on river reaches that are relatively unaffected by flow modifications from dams. Furthermore, these samples should be collected in river reaches which are not significantly influenced by mixing considerations (wastewater plumes, confluence of rivers, etc.). In addition, the sampling locations should be chosen such that they are in close proximity to HYDAT monitoring stations. This would allow for accurate estimation of flow conditions on each day of sampling.

Finally, improvements in model predictions could be gained by disaggregated sales data for the compounds of interest. For example, currently, we calculate the per capita use of compounds of interest based on sales data from Canada-wide statistics. However, sales data at the level of individual provinces or cities, or even at finer scales, is readily available. Therefore, in cases where consumption of substances differs significantly in different regions, the accuracy of our predictions could be much improved. Such data is available, albeit at a cost, from the firm IMS Health.

6.   Conclusions

Based on the results of the presented report, the following main conclusions can be distilled:

- We provided a proof-of-concept to develop a model that is capable of estimating at least the order or magnitude of chemical concentrations of down-the-drain consumer products for rivers in Quebec, Ontario and parts of contributing areas in the US.
- We have conducted a simple sensitivity analysis and mass balance validations with the data available to us.
- From the results, we are confident that the model is capable to be used to screen chemicals for possible risks for the environment and public health.
- Our model predicts chemical concentrations within a factor of 5 or better, which is sufficient for screening purposes where the performance goal tends to be within an order of magnitude.
- However, the performance of the model has not been established more quantitatively due to the lack of adequate in-river concentration measurements.

We believe that the presented model can be expanded towards a pan-Canadian scale. For that purpose, and for general model improvement, we recommend to:

- Integrate WWTPs for other Canadian provinces and for contributing parts of the U.S.
- Improve the large-scale river discharge model by implementing updated runoff estimates; adapt the model for Canada-specific characteristics (cold-climate hydrology) and optimize it for the required purposes (calculation of low flows); continue the evaluation process by using gauging stations for all of Canada.
- Improve the mass balance validations using a set of in-stream measurements based on a dedicated measurement campaign.
- Further explore uncertainty of the input parameters and develop best practices to describe the uncertainty of the model.
- Conduct more research to better understand removal processes of key contaminants during the treatment process.
- Integrate locations of water intake points, co-registered to associated river reaches, to conduct risk assessments for drinking water sources.
- Perform a comprehensive network analysis to identify the treatment plants with the highest impact on water quality.
- Develop scenarios for identification of target intervention areas.
- Develop new indicators to assess trends in large-scale water quality associated with WWTPs.
- Develop a web-based platform to communicate the results, similar to ISTREEM and Great-ER 3.0.

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Annex

A1. **Flow regime examples and Nash–Sutcliffe Efficiency (NSE) rating**
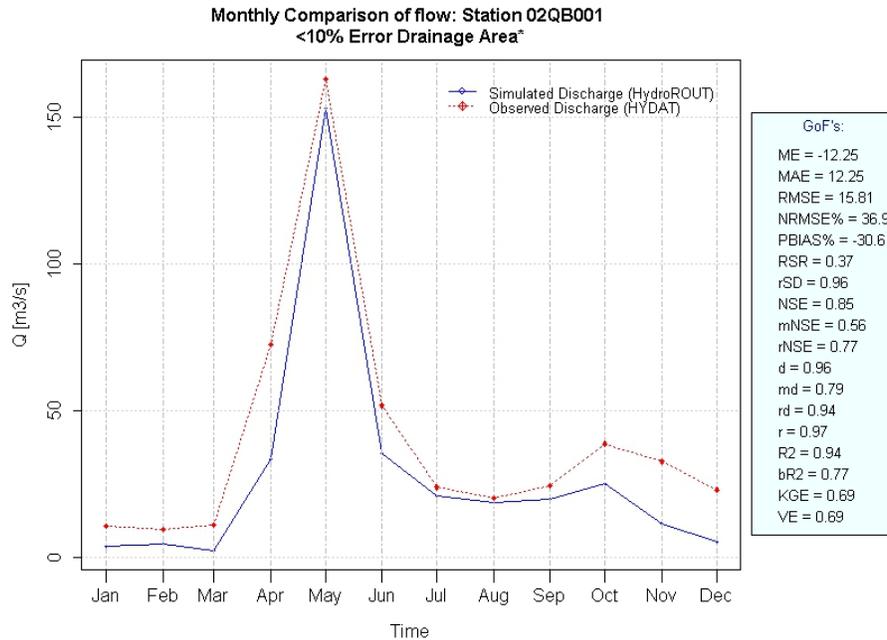

Figure A-1: NSE rating example: Very Good fit
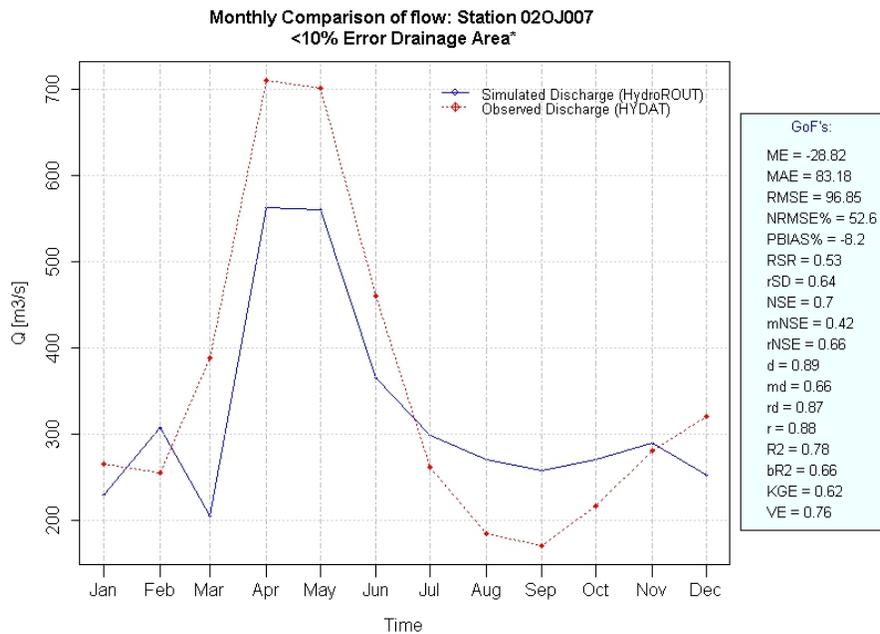
Figure A-2: NSE rating example: Good fit
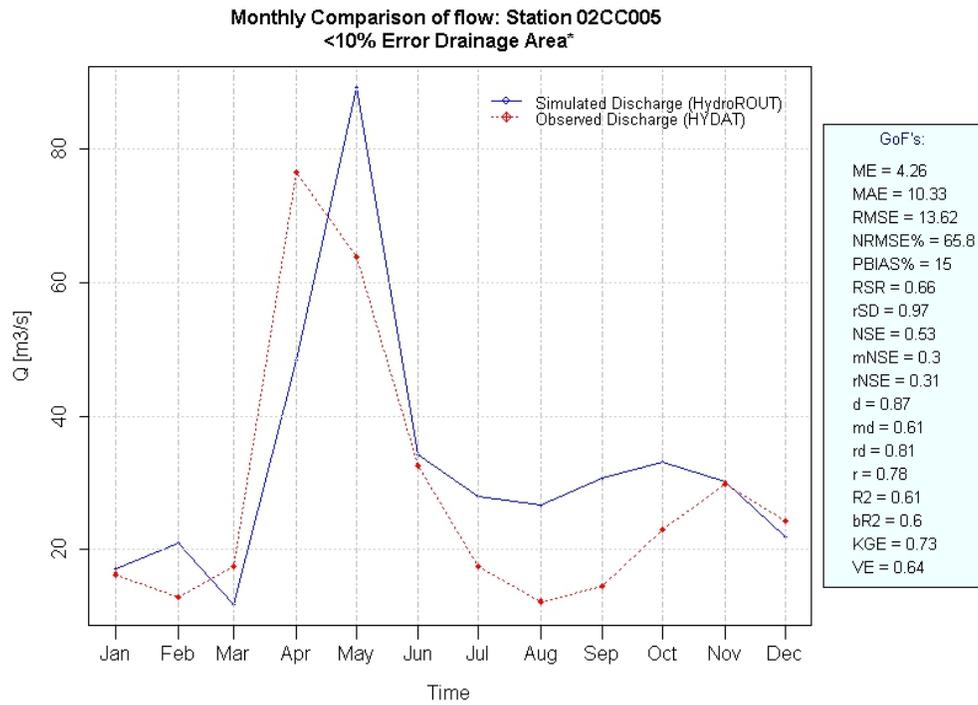
Figure A-3: NSE rating example: Satisfactory fit
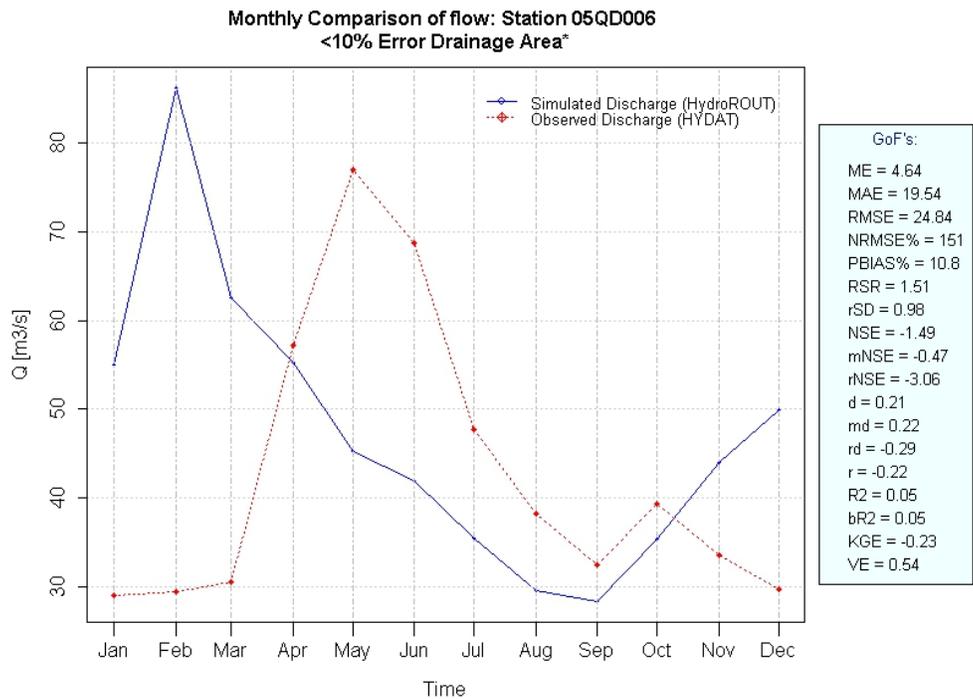
Figure A-4: NSE rating example: Unsatisfactory fit

A2. Discharge Validation

Table A-1: Statistics for low flow (Q90-Month) validation using different sets of HYDAT gauging stations with different characteristics (for corresponding scatterplots see Figure A-5 below).

Set	Max. upland error (%)	Years of data	R^2	Number of stations
A	10	10	0.89	307
B	10	30	0.92	97
C	25	10	0.88	367
D	25	30	0.91	111
E	100	10	0.43	458
F	100	30	0.35	138

Table A-2: Statistics for long-term average flow validation using different sets of HYDAT gauging stations with different characteristics (for corresponding scatterplots see Figure A-6 below).

| Set	Max. upland Error (%)	Years of data	R^2	Number of stations
G	10	10	0.97	307
H	10	30	0.97	97
I	25	10	0.97	367
J	25	30	0.97	111
K	100	10	0.40	458
L	100	30	0.31	138
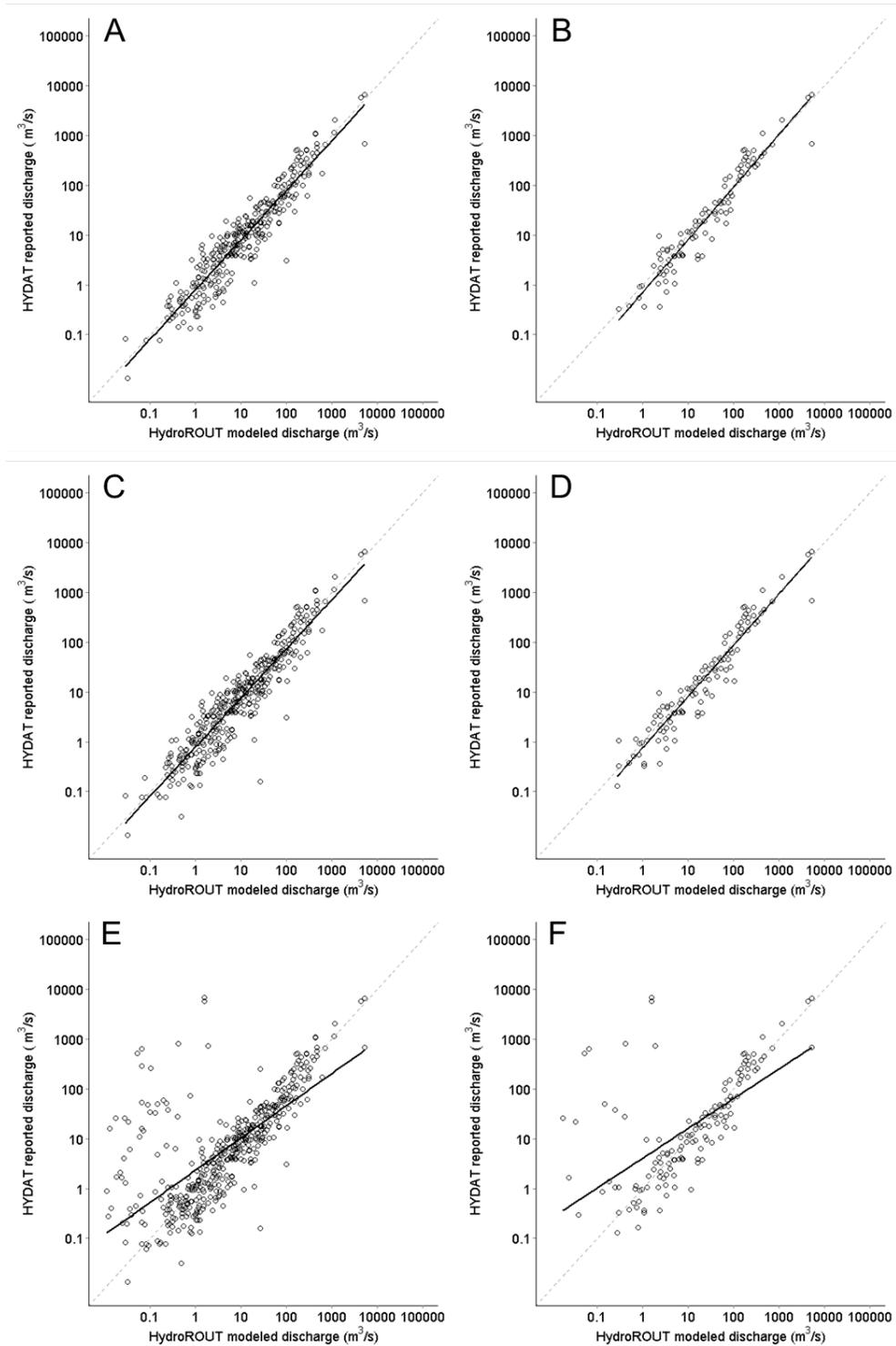
Figure A-5: Scatterplots for observed and modeled low flow (Q90-Month) values (see Table A-1 for more explanation). Plots E and F include stations with large discrepancies in reported versus modeled watershed areas; these HYDAT stations may either be co-registered to incorrect tributaries on the HydroSHEDS river network, or may be located on braided stream channels (or canals) which are not properly represented in HydroSHEDS.
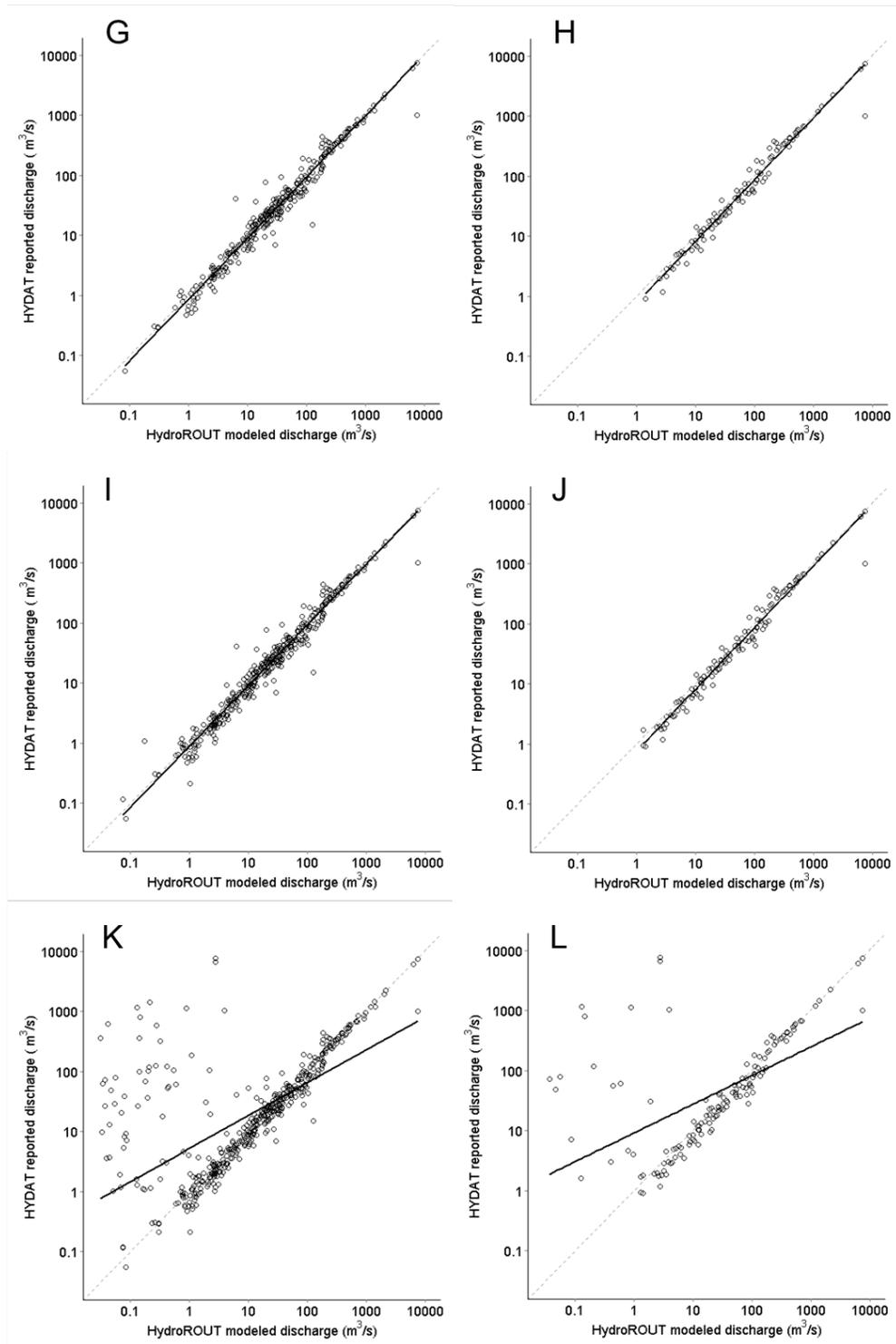
Figure A-6: Scatterplots for observed and modeled long-term average flow values (see Table A-2 for more explanation). Plots K and L include stations with large discrepancies in reported versus modeled watershed areas; these HYDAT stations may either be co-registered to incorrect tributaries on the HydroSHEDS river network, or may be located on braided stream channels (or canals) which are not properly represented in HydroSHEDS.